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ANNUAL REPORTS
ON THE
PROGRESS OF CHEMISTRY

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1915.

ISSUED BY THE CHEMICAL SOCIETY.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>A.</i>	Abstracts in Journal of the Chemical Society.*
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i>	Annals of Botany.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim. Applicata</i>	Annali di Chimica Applicata.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>Ann. Inst. Pasteur</i>	Annales de l'Institut Pasteur.
<i>Ann Physik</i>	Annalen der Physik.
<i>Ann. Physique</i>	Annales de Physique.
<i>Ann. Report</i>	Annual Reports of the Chemical Society.
<i>Apoth.-Zeit.</i>	Apotheker Zeitung.
<i>Arch. Int. Med.</i>	Archives of Internal Medicine.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arkiv. Kem. Min. Geol.</i>	Arkiv för Kemi. Mineralogi och Geologi.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i>	Berichte der Deutschen physikalischen Gesellschaft.
<i>Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Biochem. Bull.</i>	Biochemical Bulletin.
<i>Biochem. J.</i>	The Biochemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Centr. Bakt. Par.</i>	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Centr. Min.</i>	Centraleblatt für Mineralogie, Geologie und Palaeontologie.
<i>Chem. News</i>	Chemical News.
<i>Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Gummi-Zeit.</i>	Gummi-Zeitung.
<i>Inter. Zeitsch. Phys.-chem. Biol.</i>	Internationale Zeitschrift für physikalisch-chemische Biologie.
<i>Jahrb. Radioaktiv. Elektronik</i>	Jahrbuch der Radioaktivität und Elektronik.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.

* The year is not inserted in references to 1915.

ABBREVIATED TITLE.	JOURNAL.
<i>J. Amer. Chem. Soc.</i> . . .	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i> . . .	Journal of Biological Chemistry, New York.
<i>J. Bd. Agric.</i> . . .	Journal of the Board of Agriculture.
<i>J. Ind. Eng. Chem.</i> . . .	Journal of Industrial and Engineering Chemistry.
<i>J. Pharm. Chim.</i> . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . .	Journal of Physiology.
<i>J. pr. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Roy. Agric. Soc.</i> . . .	Journal of the Royal Agricultural Society.
<i>J. Russ. Phys. Chem. Soc.</i> . . .	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i> . . .	Journal of the Society of Chemical Industry.
<i>J. Washington Acad. Sci.</i> . . .	Journal of the Washington Academy of Sciences.
<i>Kolloid-Zeitsch.</i> . . .	Kolloid-Zeitschrift.
<i>Landw. Versuchs-Stat.</i> . . .	Die landwirtschaftlichen Versuchs-Stationen.
<i>Monatsh.</i> . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. Sci.</i> . . .	Moniteur scientifique de Quesneville.
<i>Nuovo Cim.</i> . . .	Il Nuovo Cimento.
<i>Pharm. J.</i> . . .	The Pharmaceutical Journal.
<i>Pharm. Weekblad</i> . . .	Pharmaceutisch Weekblad.
<i>Phil. Mag.</i> . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Physikal. Zeitsch.</i> . . .	Physikalische Zeitschrift.
<i>P.</i> . . .	Proceedings of the Chemical Society.
<i>Proc. Camb. Phil. Soc.</i> . . .	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam.</i> . . .	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i> . . .	Proceedings of the National Academy of Sciences, Washington.
<i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.
<i>Rec. trav. chim.</i> . . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Sci. Proc. Roy. Dubl. Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> . . .	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Staz. sper. agrar. Ital.</i> . . .	Stazioni sperimentali agrarie Italiani.
<i>T.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i> . . .	Transactions of the Faraday Society.
<i>Trans. Roy. Soc. Canada</i> . . .	Transactions of the Royal Society of Canada.
<i>Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Biol.</i> . . .	Zeitschrift für Biologie.
<i>Zeitsch. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . . .	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. wiss. Mikroskop.</i> . . .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

IN accordance with the practice followed by previous writers, the present Report deals only with certain selected topics. The work under review covers a considerable number of papers published in Continental journals during the second half of 1914, and, in these circumstances, the volume of original research falling within the scope of this Report is probably not less, but appreciably greater, than the average of recent years. Lack of space is alone responsible for the omission of any reference to many interesting and important papers.

Atomic Structure and Line Spectra.

The success achieved by Bohr in the explanation of the series spectra of hydrogen and helium by application of the quantum hypothesis to Rutherford's model of the atom was described in last year's Report.¹ In view of this development of the theory of atomic structure, which in a more recent paper² has been shown to offer an interpretation of the results obtained by Stark³ for the effect of an electrical field on the hydrogen spectrum, of the relations exhibited by the high-frequency spectra of the elements, and of the minimum voltages required to produce spectral lines (see p. 2), the spectra of hydrogen and helium have acquired a very special interest, and various problems relating to the emission spectra of these elements have been examined. The difficulty of differentiating between the lines of the two elements has led to much confusion, which is mainly due to the fact that the helium

¹ *Ann. Report*, 1914, 5.

² N. Bohr, *Phil Mag.*, 1915, [vi], **30**, 394; *A.*, ii, 682.

³ J. Stark, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 932; *A.* 1914, ii, 2.

spectrum usually shows the hydrogen lines. Under suitable conditions the hydrogen lines can be eliminated, and as the result of accurate measurements⁴ in such a helium spectrum, it has been shown that the series spectrum of hydrogen consists only of lines which are given by $\nu = 109704(1/n_1^2 - 1/n_2^2)$, and that the series spectrum of helium consists, in addition to the ordinary helium lines, of all the lines represented by

$$\nu = 109750(1/(n_{1/2})^2 - 1/(n_{2/2})^2).$$

This series includes both the Pickering lines and the helium lines predicted by Bohr on the basis of his theory of the constitution of the helium atom.

The difference between the Balmer series of hydrogen lines and the series represented by the second formula is brought out in a very striking manner by some recent experiments⁵ on the minimum voltage which is necessary for the production of spectral lines. Whilst about 13 volts suffice for the excitation of the Balmer series, it has been found that about 80 volts are required to excite the second series. These voltages agree closely⁶ with the values, which, according to Bohr's theory, are required for the removal of the electron from the hydrogen atom and of the two electrons from the helium atom, namely, 13.6 and 81.3 volts respectively.

Very exact measurements⁷ of the wave-lengths of the first six lines of the hydrogen series have shown that these cannot be exactly represented by Balmer's formula. It follows that Bohr's theory does not give a complete account of the spectral relations of the hydrogen atom, and some interesting attempts have been made to account for the discrepancy. The supposition that the nucleus or core of the atom gives rise to a magnetic field equivalent to that set up by five (or six) magnetons is said⁸ to yield results which are in agreement with the observations of Curtis. This hypothesis is criticised by Bohr,⁹ who considers that the doubling of the hydrogen lines makes it almost impossible to place any definite interpretation on such small differences as are actually involved in the comparison between experiment and the Balmer formula. Since the components of the doublets are of unequal intensity, and the distance between the components is much greater than the deviations from the requirements of the formula in question, arguments which are based on the measurement of the "centre of gravity" of

⁴ E. J. Evans, *Phil. Mag.*, 1915, [vi], **29**, 284; *A.*, ii, 77; J. Stark and G. Wendt, *Ann. Physik*, 1914, [iv], **43**, 983; *A.*, 1914, ii, 314.

⁵ Rau, *Ber. Deut. physikal. Ges.*, 1914, **16**, 468.

⁶ N. Bohr, *Phil. Mag.*, 1915, [vi], **30**, 394; *A.*, ii, 682.

⁷ W. E. Curtis, *Proc. Roy. Soc.*, 1914, [A] **90**, 605; *A.*, 1914, ii, 761.

⁸ H. S. Allen, *Phil. Mag.*, 1915, [vi], **29**, 40, 140; *A.*, ii, 33; *ibid.*, 1915, [vi], **29**, 714; *A.*, ii, 439.

⁹ N. Bohr, *ibid.*, 332; *A.*, ii, 92.

the lines cannot carry great weight. It is suggested that the doubling may be due to slight ellipticity of the orbits of the electron.

Spectra of Metallic Vapours.

Many difficulties have to be surmounted before the principles underlying Bohr's theory can be applied to the deduction of the spectra of elements of higher atomic weight. Much progress has been made, however, in the experimental investigation of line spectra, and in various ways evidence has been obtained which shows that different line series are attributable to different carriers or centres. In some cases it has been possible to determine the nature of these centres and the conditions which give rise to the characteristic radiations.

The fact that the vapours of certain metals (mercury, cadmium, zinc) give rise under certain conditions to spectra which consist of a single line would seem to be of very special significance. The wave-lengths of these lines are λ 2536.72 for mercury, λ 3260.17 for cadmium, and λ 3075.99 for zinc. The emission of these single-line spectra occurs when the vapours of the metals are traversed by electrons the energy of which falls between definite limits. According to J. C. McLennan and J. P. Henderson,¹⁰ the single line spectra are replaced by multiple-line spectra when the arcing potentials exceed 12.5 volts in the case of mercury, 15.3 volts for cadmium, and 11.85 volts for zinc. The lower limiting values of potential which give rise to the single-line spectra correspond in all probability with the minimum ionisation potentials, and in the case of mercury it has been shown by J. Franck and G. Hertz¹¹ that the minimum potential (4.9 volts) is almost identical with that calculated from the frequency of the single-line emission on the basis of the quantum theory. Corresponding data for cadmium and zinc are not yet available, but the agreement between the observed and calculated ionisation potentials in the case of mercury cannot be regarded as accidental, and further evidence is thereby obtained in support of the quantum theory in its application to radiation phenomena.

If an arc discharge is passed through the vapours of metals in the course of distillation, the excited luminosity remains visible for an appreciable time after the vapour has left the region of the arc. Experiments¹² with the vapours of mercury, sodium, potassium, calcium, magnesium, zinc, cadmium, and thallium have shown

¹⁰ *Proc. Roy. Soc.*, 1915, [A], **91**, 485; *A.*, ii, 657.

¹¹ *Ber. Deut. physikal. Ges.*, 1914, **16**, 457; *A.*, 1914, ii, 515.

¹² (Hon.) R. J. Strutt, *Proc. Roy. Soc.*, 1913, [A], **88**, 110; *A.*, 1913, ii, 279; *ibid.*, [A], **90**, 364; *A.*, 1914, ii, 599; *ibid.*, 1914, [A], **91**, 92; *A.*, ii, 41.

that the line spectra are completely extinguished when the luminous jet of vapour is passed through a negatively electrified net, indicating that the luminous centres are positively charged ions. In some cases (sodium, magnesium, zinc) the lines of one series are more readily extinguished than those of another. In this way it has been shown, for example, that the centres of emission of the subordinate series of sodium lines are not identical with those which give rise to the *D* line. It has not been possible as yet to identify the carriers of the line series, and in the light of observations on sodium vapour, in which the luminosity excited by electric discharge has been compared with that excited by the radiation from a sodium flame, it would seem that the relations are somewhat involved. The persistence of the electrically excited luminosity is much greater than that of the fluorescent emission. On the other hand, this marked difference in persistence is not observed with mercury vapour when this is subjected to the action of these two exciting agents.

It has been known for some time that sodium vapour excited by *D*-light emits rays of the same frequency, and it has now been shown¹³ that excitation by the second member of the principal series of lines (λ 3303) also gives rise to the lateral emission of the *D*-line. In these circumstances there is no measurable radiation of ultraviolet light of the exciting frequency or of the lines of the subordinate series. If the less refrangible component of the λ 3303 doublet is used as the exciting source, both the *D*-lines are emitted in approximately the same intensity. This is rather remarkable in view of the fact that no emission of D_1 is observed when sodium vapour is stimulated by D_2 .¹⁴

The elucidation of the nature of the centres of emission responsible for the different spectra given by an element under different conditions has been one of the chief objects of a detailed study of canal-ray spectra by J. Stark and his collaborators in experiments which have been carried on for a number of years.¹⁵ The high velocity of the canal rays gives rise to a Doppler effect, and the study of this in relation to the electrical conditions of the discharge affords a means of differentiating between the charged carriers of the luminosity. The absence of a Doppler effect in any series of lines is considered to show that the emission centres consist of electrically neutral particles. To take the case of helium, which is of special interest in view of the fact that the two distinct

¹³ (Hon.) R. J. Strutt, *Proc. Roy. Soc.*, 1915, [*A*], **91**, 388; *A.*, ii, 399.

¹⁴ R. W. Wood and L. Dunoyer, *Phil. Mag.*, 1914, [vi], **27**, 1018.

¹⁵ Compare J. Stark, *Physikal. Zeitsch.*, 1913, **14**, 1012; *A.*, 1913, ii, 172; J. Stark, G. Wendt, and M. Kirschbaum, *ibid.*, 1913, **14**, 770; *A.*, 1913, ii, 813; J. Stark and R. Künzer, *Ann. Physik.*, 1914, [iv], **45**, 29; *A.*, ii, 202.

groups of line series were at one time¹⁶ attributed to two different elements, it has been shown that the principal and the two subsidiary series of doublets are due to helium atoms with a single positive charge, whilst the principal and subsidiary series of simple lines are to be attributed to helium atoms with a double charge.

In general, the observations on canal-ray spectra show that the distinction, which is usually made between the arc and spark lines of an element, corresponds with a real difference in origin, in that the arc lines are due to particles which carry a single charge and move relatively slowly in an electrical field, whereas the spark lines are due to multivalent ions of relatively greater speed.¹⁷ The results obtained by this method of analysis are for the most part in agreement with those furnished by Thomson's method¹⁸ of electromagnetic analysis.

The luminosity resulting from the bombardment of gases by cathode rays has been found to vary in the sense that the colour of the emitted light changes from blue to red when the speed of the cathode rays is reduced.¹⁹ This method of experiment has been applied successfully in the investigation of the conditions which give rise to the emission of banded spectra by different gases.²⁰

A simple method of obtaining the glow discharge through metallic vapours has been described,²¹ and observations made with this apparatus show the existence of a close similarity between the negative glow and the spark spectrum on the one hand, and between the positive glow and the arc spectrum on the other.

Absorption Spectra.

The study of absorption spectra continues to attract a great deal of attention. Much of this work has been directed to the determination of the influence of substitution in the benzene ring,²² and to the elucidation of the structure of organic compounds,²³ but solutions of inorganic substances have also been examined.²⁴

¹⁶ C. Runge and F. Paschen, *Phil. Mag.*, 1895, [ii], **40**, 297; *A.*, 1896, ii, 1.

¹⁷ J. Stark, *Physikal. Zeitsch.*, 1913, **14**, 961; *A.*, 1913, ii, 1103.

¹⁸ (Sir) J. J. Thomson, *Phil. Mag.*, 1912, [vi], **24**, 209; *A.*, 1912, ii, 885.

¹⁹ E. Gehecke and R. Seeliger, *Ber. Deut. physikal. Ges.*, 1912, **14**, 335; *A.*, 1912, ii, 517.

²⁰ R. Seeliger, *Physikal. Zeitsch.*, 1915, **16**, 55; *A.*, ii, 117.

²¹ L. Janicki and R. Seeliger, *Ann. Physik.*, 1914, [iv], **44**, 1151; *A.*, ii, 195.

²² Compare J. E. Purvis, *T.*, 1915, **107**, 496; *A.*, ii, 299; *T.*, 1915, **107**, 966, *A.*, ii, 607.

²³ N. A. Waliaschko and Miss M. V. Boltina, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1741, 1780, 1788, 1822; *A.*, ii, 393-398.

²⁴ C. S. Garrett, *T.*, 1915, **107**, 1324; *A.*, ii, 714; K. Schaefer, H. Nigemann, and W. Köhler, *Zeitsch. Elektrochem.*, 1915, **21**, 181; *A.*, ii, 389.

For the most part, use is made of the Hartley-Baly method, absorption curves being plotted from the photographic records so as to show the position and depth of the selective absorption bands. Greater interest attaches to observations in which the absorption curves are based on spectro-photometric measurement of the extinction-coefficients, and it is satisfactory to note that such determinations form the basis of a considerable proportion of the more recent work on absorption spectra.

It was at one time supposed that the aliphatic ketones show the same selective absorption band, that the persistence of this varies from one ketone to another, and that there is a connexion between the persistence of the characteristic band and the reactivity of the ketone. This view has been shown to be entirely erroneous, and the further investigation of the absorption spectra of these ketones, carefully purified by conversion into the sodium hydrogen sulphite compounds or the semicarbazones, has shown²⁵ that the centre of the absorption bands is not invariable, but varies appreciably according to the number of methyl groups which are present in the α - and β -positions relative to the carbonyl group. The molecular extinction-coefficient has, however, the same value for twelve out of the fifteen ketones examined. The spectral relations thus brought to light differ entirely from those indicated by earlier observations, and although the divergence may be partly attributable to the greater purity of the materials used in the later experiments, it seems probable that the transition from more or less qualitative to quantitative methods of measuring the absorption is largely responsible for the difference in the results.

By comparison of the extinction curves of twenty-two mono-substituted benzene derivatives it has been shown²⁶ that the reactivity of these compounds is reflected in a general way in the absorption spectra. With three exceptions, those compounds which give meta-disubstituted derivatives show absorption bands of very small persistence, whilst those which give ortho- and para-disubstitution products exhibit deep bands of large persistence. It would therefore seem possible to anticipate the result of further substitution in the benzene ring by an examination of the absorption of the mono-substituted derivative.

Up to the present, the absorption spectra of compounds have afforded no evidence of exact numerical relations comparable with those which are exhibited by the series lines in the emission spectra of the elements. That regularities of a simple character do exist

²⁵ F. O. Rice, *Proc. Roy. Soc.*, 1914, [A], **91**, 76; *A.*, ii, 35.

²⁶ E. C. C. Baly and F. G. Tryhorn, *T.*, 1915, **107**, 1058; *A.*, ii, 606.

is shown by recent observations of Baly and his co-workers.²⁷ According to these results, the frequencies of the centres of the absorption bands of a given compound are integral multiples of a fundamental frequency in the short-wave ultra-red. By application of the quantum hypothesis to the phenomena of absorption and fluorescence the conclusion is drawn that if ν_0 is the fundamental frequency, energy can also be absorbed (or emitted) at the frequencies $\nu_1, \nu_2, \nu_3 \dots$, where $\nu_1, \nu_2, \nu_3, \dots$ are successive integral multiples of ν_0 . If m and $m+n$ are integers and ν_m and ν_{m+n} the corresponding frequencies, then ν_0 may be derived from the equation $\nu_0 = (\nu_{m+n} - \nu_m) / n$.

The available evidence is apparently favourable to this theory, although it would seem necessary to assume that there are two or more fundamental frequencies in order to account for the spectra which have been examined up to the present.²⁸ The assumption of two or more characteristic constants affords an explanation of the fact that certain bands are of much greater intensity than others, in that specially marked absorption is to be expected when the frequency is either an even multiple of the several fundamental frequencies or represents the least common multiple of these numbers. By way of criticism, it may be urged that the multiplication of fundamental frequencies in the infra-red will ultimately lead to such a large number of multiple frequencies in the ultra-violet, that ultra-violet absorption of any desired wave-length may be approximately represented in terms of the theory.

In actual practice, the absorption of most substances can only be examined in solution, and the relations between the frequencies of the absorption bands are not so simple, for the position of these bands is to some extent dependent on the nature of the solvent and the concentration of the solution. It is only when the molecules of a substance are unacted on by other molecules, as when the substance is in the form of vapour, that the above frequency relations can be considered as exact.

The displacement of the absorption bands of a substance under the influence of a solvent was for some time supposed to be connected with the refractive index of the medium (Kundt's rule). This view is, however, quite untenable, and according to Baly the observed shifts of the absorption bands are causally related to the displacement of the fundamental vibration which is determined by the relative affinity between solute and solvent. The evidence at present available²⁹ indicates that when a solvent is

²⁷ E. C. C. Baly, *Phil. Mag.*, 1914, [vi], **27**, 632; *A.*, 1914, ii, 318; *ibid.*, 1915, [vi], **29**, 223; *A.*, ii, 77. ²⁸ E. C. C. Baly, *ibid.*, 1915, **30**, 510; *A.*, ii, 714.

²⁹ E. C. C. Baly and F. G. Tryhorn, *T.*, 1915, **107**, 1121; *A.*, ii, 605.

added in gradually increasing quantity to a given substance its absorption bands are displaced at first towards the red until a minimum frequency is reached. Further dilution brings about a progressive shift of the centres of the absorption bands towards shorter wave-lengths until at great dilution a maximum frequency is attained, which is identical with the frequency characteristic of the substance in the state of vapour.

The possibility of locating the absorption bands of organic substances has also been discussed from an entirely different point of view.³⁰ It is assumed that the absorption is due to the valency electrons which move in circular orbits round a central nucleus, the radii of the orbits depending on the mode of combination of the atoms in the molecule. Mutual interaction between the various electrons will take place, and the location of absorption bands is consequently reduced to compounding such actions in accordance with the principles of mutual induction. By the application of this method it has been possible to locate the position of the absorption bands in a variety of organic substances.

Molecular Complexity of Pure Liquids.

The significance to be attached to the temperature-coefficient of the molecular surface energy of a liquid has undergone appreciable alteration since attention was first directed to this factor by Eötvös and by Ramsay and Shields. It is now generally admitted that the constancy of the temperature-coefficient, and not its absolute value, is the essential characteristic of normal liquids or of liquids the complexity of which is independent of the temperature. In general, for such liquids the coefficient decreases slightly with rise of temperature.

Attention has been recently drawn³¹ to the function $(\gamma - t \cdot d\gamma/dt)(Mv)^{\frac{2}{3}}$, which represents the total molecular surface energy and, for liquids previously recognised as normal, has a nearly constant value over a range of temperature that extends almost to the critical temperature. On the other hand, for associated substances, like water and the alcohols, the association of which varies with the temperature, the total molecular surface energy increases rapidly and continuously with rise of temperature. In regard to the relation between the total and free molecular surface energy, $\gamma(Mv)^{\frac{2}{3}}$, it is obvious that this follows at once from the Helmholtz equation, $A - U = t dA/dt$.

A redetermination³² of the surface tension of acetic acid between

³⁰ N. P. McClelland, *Phil. Mag.*, 1915, [vi], **29**, 192; *A.*, ii, 34.

³¹ G. M. Bennett and A. D. Mitchell, *Zeitsch. physikal. Chem.*, 1913, **84**, 475; *A.*, 1913, ii, 927.

³² G. M. Bennett, *T.*, 1915, **107**, 351; *A.*, i, 212.

15° and 150° has shown that the temperature-coefficient of the free surface energy falls slightly with rise of temperature, and that the total surface energy remains nearly constant. Its behaviour resembles closely that of a normal liquid, and the conclusion is drawn that it consists at all temperatures exclusively of molecules of the formula $(\text{CH}_3 \cdot \text{CO}_2\text{H})_2$. The evidence afforded by other criteria is not inconsistent with this view.

Reference may here be made to an extensive series of measurements of the surface tensions of homologous series of organic compounds and of fused inorganic salts,³³ which cover a wide range of temperature.

Binary Liquid Mixtures.

The question of the interpretation of property-composition curves is far from being settled. Comparison of the freezing point and viscosity curves shows³⁴ that the formation of solid compounds is not always accompanied by viscosity maxima (or minima), although pairs of substances which form a compound in the solid state occasionally exhibit a corresponding maxima on the viscosity-composition curve. The liquid mixture for which the observed viscosity shows a maximum deviation from the requirements of the simple mixture rule also differs very frequently from the composition of the compound, which is indicated by freezing-point measurements.³⁵ Formamide, for example, forms the solid compound $\text{H} \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$ with water, but the maximum deviation occurs at 40 mols. per cent. of formamide. With acetic acid it forms the solid compound $\text{H} \cdot \text{CO} \cdot \text{NH}_2 \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{H}$, whereas the maximum deviation is found at 50 mols. per cent. of formamide. Furthermore, it may be noted that ethyl alcohol and water form no definite compound according to freezing-point measurements,³⁶ although mixtures of these liquids yield a viscosity-composition curve with a very strongly developed maximum, and both the viscosity and specific volume curves show maximum deviation from the mixture rule at the composition $\text{C}_2\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}$. The composition corresponding with this maximum deviation is, moreover, independent of the temperature over a considerable range.

In comparing freezing points with other properties of liquid

³³ F. M. Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 329; *A.*, 1914, ii, 805; F. M. Jaeger and M. J. Smit, *ibid.*, 1914, **17**, 365; *A.*, 1914, ii, 805; F. M. Jaeger and J. Kahn, *ibid.*, 1915, **18**, 269; *A.*, ii, 747.

³⁴ I. Kurnakov, D. Krotkov, and M. Oksman, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 558; *A.*, ii, 524.

³⁵ S. English and W. E. S. Turner, *T.*, 1915, **107**, 774; *A.*, ii, 525.

³⁶ N. A. Puschin and (Miss) A. A. Glagoleva, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 100; *A.*, ii, 243.

mixtures it should, however, be remembered that differences in the temperatures involved may be to some extent responsible for the apparent discrepancies, in that compounds which exist in the liquid mixture in the neighbourhood of the freezing point may dissociate very rapidly as the temperature rises.

Molecular Kinetics.

In view of the fact that recent observations lend considerable support to the view that the molecules are real physical entities, the investigation of the mechanism of processes which involve the exchange of molecules at boundary surfaces has acquired new interest. Such processes are evaporation, sublimation, dissolution, and crystallisation. By applying the kinetic theory to the molecular exchange at the surface of contact between a liquid (or solid) and its vapour, it can be shown³⁷ that the maximum rate of evaporation in a vacuum, as measured by the rate of change in the level of the surface of the liquid or solid, is given by the formula $V = k \cdot \sqrt{M/T} \cdot (P - p)/d$, in which P is the vapour pressure at temperature T , p the actual pressure of the vapour, M the molecular weight of the substance, d its density, and k a constant $= 4.38 \times 10^{-5}$. This maximum rate corresponds with the total number of molecules which impinge on the liquid surface in unit time.

Actual measurements of the rate of evaporation have given much smaller values, and from this it is inferred that only a fraction of the molecules which impinge on the surface of the liquid are absorbed. If v is the observed rate of evaporation, then $N = V/v$ represents the ratio of the total number of molecules which come into contact with the surface to the number which are absorbed. It is remarkable that N decreases rapidly with rise of temperature—for nitrobenzene from 15 at 40° to 4 at 65°, for naphthalene from 28 at 40° to 7.4 at 70°, and for iodine from 18 at 40° to 4.8 at 70°. The extent to which the results are vitiated by differences between the temperature of the liquid surface and that of the surroundings is difficult to estimate, but the author is of the opinion that the temperature effect is definitely established.

The investigation of the molecular exchange at solid-liquid boundary surfaces in thermodynamic equilibrium has been rendered possible by an ingenious device,³⁸ which consists in the addition to the liquid or solid phase of a minute quantity of a radioactive substance isotopic with the substance under examination. By

³⁷ R. Marcellin, *Ann. Physique*, 1915, [ix], 3, 185; A., ii, 328.

³⁸ G. von Hevesy, *Physikal. Zeitsch.*, 1915, 16, 52; A., ii, 156.

impregnating crystals of lead chloride with thorium-*B* and measuring the radioactivity of the solution after measured intervals of time, data have been obtained which afford a measure of the rate of exchange of molecules at the surface of lead chloride in contact with its saturated aqueous solution. Radioactive isotopes have also been used³⁹ in the investigation of the phenomenon of dissolution of solids in liquids when the thickness of the layer of solid is of molecular dimensions. The process appears to be governed by the same laws which have been shown to apply in the dissolution of ordinary solids.

The Temperature-coefficient of Chemical Change.

The difficulties associated with the explanation of the high value of the temperature-coefficient of chemical reaction in terms of the kinetic theory are too well known to need any introductory reference to the points at issue. The hypothesis that there are two kinds of molecules, active and inactive, and that the observed change in the velocity of reaction is mainly due to the displacement of the equilibrium between the two molecular species, has never met with a very favourable reception. It is now suggested⁴⁰ that the active molecules are those which have a total energy-content equal to or greater than a certain limiting value. This limiting value represents the critical energy, and the difference E between the critical energy and the average energy of the molecules determines the influence of temperature on the velocity of reaction k in accordance with the equation $d \log k / dT = E / RT^2$, which is of the same form as the equation given by Arrhenius.

The connexion between velocity of reaction and temperature has also been discussed by Sutton,⁴¹ who, on the basis of the mass law and a thermodynamic relation given by Gibbs and Planck, arrives at an expression for the velocity of reaction from which it would appear that the number of effective collisions between the reacting molecules varies with the temperature θ according to some function which involves $e^{-A/\theta}$, where A is a constant. The mechanism consistent with this is limited to two alternatives: (1) that reacting molecules must collide with a relative velocity of approach which exceeds a certain limiting value, (2) that reaction is limited to molecules with velocities between limits v and $v + \delta v$. The fact that unimolecular reactions are influenced by change of temperature to the same extent as reactions of higher order suggests that the

³⁹ G. von Hevesy, and Miss E. Rona, *Zeitsch. physikal. Chem.*, 1915, **89**, 294; *A.*, ii, 247.

⁴⁰ R. Marcelin, *Ann. Physique*, 1915, [ix], **3**, 120; *A.*, ii, 328.

⁴¹ T. C. Sutton, *Phil. Mag.*, 1914, [vi], **28**, 798; *A.*, ii, 14.

molecules concerned owe their reactivity to collisions between atoms in the molecule which satisfy one or other of these conditions.

Soret's Phenomenon.

If two portions of the same solution are maintained at different temperatures, some of the dissolved substance diffuses from the hot to the cold solution, as was first observed by Soret. This is in agreement with the osmotic theory, according to which the ratio of the concentrations of the hot and cold solutions, when equilibrium is attained, should be in the inverse ratio of the absolute temperatures. Many difficulties are met with in the quantitative investigation of this phenomenon, and previous experiments of Arrhenius⁴² led to no very conclusive result, except in so far as they showed that the results anticipated by theory were seldom realised in practice. In a series of new experiments,⁴³ a considerable improvement of technique has been realised, in that the length of the columns of the hot and cold solutions was reduced from 15 cm. to 1.5 cm., resulting in a large reduction of the time required for the attainment of equilibrium.

The results obtained with this apparatus show that the ratio of the equilibrium concentrations varies with the concentration of the original solution. Sometimes the observed ratio is greater than the theoretical, but decreases with falling concentration. This behaviour is shown by sodium hydroxide, copper sulphate, and antipyrine. On the other hand, for sodium chloride, sucrose, and glycerol the observed is less than the theoretical ratio, and increases with falling concentration. By extrapolation to zero concentration a limiting value of the ratio is obtained, which sometimes, although by no means generally, approximates fairly closely to the theoretical ratio. The most remarkable result of these experiments, however, is afforded by the observations made with aqueous solutions of ethyl alcohol, acetone, boric acid, and aniline, for these lead to the conclusion that the temperature-gradient has no influence on the spacial distribution of these substances in dilute solution.

The above facts indicate that diffusion across the temperature-gradient is not, as a rule, solely determined by osmotic forces. On the assumption that the movements of the molecules are of the Brownian type, it is shown⁴⁴ that the distribution of the solute between the hot and cold layers should be given by the equation $c/c' = \sqrt{u'T'/uT}$, in which u and u' are the mobilities of the molecules of solute at temperatures T and T' , and c and c' are the

⁴² *Öfersigt öfver Kongl. Vetensk. Förh.*, 1893, 61.

⁴³ T. Wereide, *Ann. Physique*, 1914, [ix], 2, 55; *A.*, ii, 150.

⁴⁴ T. Wereide, *ibid.*, 67; *A.*, ii, 151.

corresponding concentrations. This hypothesis leads to the further conclusion that c/c' will tend towards unity as the mobility of the solute molecules approximates to that of the molecules of the solvent. If, in general, both types of diffusion occur, it is possible to give an explanation of the behaviour of all the substances examined.

Colloidal Solutions: Emulsions.

It has long been the custom to speak of positive or negative colloids according to whether the colloidal particles move towards the cathode or the anode. Certain colloids, such as platinum and arsenious sulphide, are regarded as typically negative, whilst ferric hydroxide affords an example of a typical positive colloid. It is a well known fact that colloidal platinum becomes positive in a dilute solution of ferric chloride, but this change in character has been explained by the assumption that the metal particles become coated with positive ferric hydroxide formed by hydrolysis of the ferric chloride.

Recent observations on colloidal ferric hydroxide⁴⁵ show that it may be obtained either as a positive or negative colloid, and that the sign of the electrical charge is determined by the environment of the colloidal particles at birth. Colloidal solutions of the hydroxides of the multivalent metals are usually prepared by dialysis of the corresponding salt solutions, and in these circumstances adsorption of the metallic ions confers a positive charge on the particles. If, however, a dilute solution of ferric chloride is run slowly into a slight excess of a dilute solution of alkali hydroxide with constant shaking, a stable colloidal solution is obtained in which the particles of ferric hydroxide are negatively charged. The charge in this case is attributed to the adsorption of hydroxyl ions from the alkaline solution. It would thus seem that the ionic atmosphere is of fundamental importance in determining the electrical character, and therefore the general properties, of the colloid.

Whether pure colloidal solutions have a measurable electrical conductivity or whether the observed conductivity is to be attributed to the presence of traces of foreign electrolytes is a matter which has been the subject of much discussion. It is known that the mobility of colloid particles is of the same order of magnitude as that of the ions, and if Stokes's law is applicable to the motion of the colloid particles in an electrical field, it may be shown⁴⁶ that the maximum charge of a colloidal particle must be proportional to its radius. If, now, the same quantity of a metal is present in

⁴⁵ F. Powis, *T.*, 1915, **107**, 818; *A.*, ii, 567.

⁴⁶ H. Nordensen, *Kolloid Zeitsch.*, 1915, **16**, 65; *A.*, ii, 306.

two solutions, the one containing colloidal particles and the other metallic ions, it follows that the conductance due to the metal will vary inversely as the square of the radius of the conducting particles. From this relation it is possible to calculate the conductivity of a colloid in terms of its concentration and the size of the colloid particles. According to the values thus obtained, it is apparent that the conductance due to particles of average size is negligibly small, and that the relatively high values recorded for the conductivity of colloids by several observers are in all probability to be attributed to the presence of small quantities of electrolytes.

The conditions determining the stability and coagulation of oil emulsions form the subject of several recent papers. It has been found⁴⁷ that the difference of potential at the oil-water interface is of the same order of magnitude as the contact potential shown by suspended particles of colloidal metals, lycopodium, quartz, glass, etc. It varies from 0.02 to about 0.05 volt. On the addition of electrolytes, the stability of the emulsions and the contact potential both undergo alterations, the stability being greatest when the contact potential is a maximum. In agreement with Hardy's theory, it is usually assumed that the stability reaches a minimum when the contact potential vanishes, and that the complete disappearance of the difference of potential at the surface of the emulsoid or suspensoid particles (isoelectric point) is the immediate cause of coagulation. This view is, however, not consistent with the most recent observations.⁴⁸ These show that there is a critical value of the contact potential (± 0.03 volt), and if, in consequence of the addition of electrolytes, the potential difference falls below the critical value, coagulation takes place, the rate of coagulation being nearly independent of the potential. The relative quantities of uni-, bi-, ter-, and quadri-valent cations (potassium, barium, aluminium, and thorium chlorides were added to a paraffin oil emulsion) required to produce rapid coagulation are much more nearly equal to the quantities required for the setting up of the critical potential than to those which correspond with zero potential.

There appears to be some doubt as to the method which should be employed in the measurement of the coagulating power of electrolytes. Two papers⁴⁹ dealing with this question may be noted. From these it would seem that different electrolytes may

⁴⁷ R. Ellis, *Zeitsch. physikal. Chem.*, 1911, **78**, 321; *A.*, 1912, ii, 13; *ibid.*, 1912, **80**, 597; *A.*, 1912, ii, 1036.

⁴⁸ F. Powis, *ibid.*, 1914, **89**, 91, 179, 186; *A.*, ii, 137, 183.

⁴⁹ O. Hauser and A. Lewite, *Kolloid Zeitsch.*, 1915, **16**, 33; *A.*, ii, 322; H. Freundlich, *ibid.*, 1915, **16**, 36; *A.*, ii, 323.

best be compared on the basis of measurements of the velocity of coagulation.

Reversed Adsorption.

A phenomenon described as reversed adsorption has been recently studied in some detail.⁵⁰ If certain dyes, for example, new magenta, are added to colloidal solutions of mercuric sulphide or sulphur, the dye is adsorbed by the colloid and coagulation takes place. Subsequently the dye is liberated, and this reversal of the adsorption is attributed to the gradual crystallisation of the amorphous coagulate. The phenomena associated with this process are in many ways similar to those which have been observed in the study of adsorption and coagulation. Both processes are autocatalytic and greatly accelerated by rise of temperature; the velocity of both increases very rapidly with the quantity of the adsorbed substance, and in both cases retardation is produced by the addition of protective colloids.

Configuration of Molecules.

Evidence afforded by the properties of crystalline liquid solutions would seem to point to the possibility of determining and comparing the geometrical configuration of different molecules.⁵¹ The very pronounced optical anisotropy shown by crystalline liquids in a magnetic field is reflected in certain properties of the solutions, such as the electrical conductivity and the rate of diffusion of the dissolved substances. If the anisotropy is measured by the ratio of the conductivities or velocities of diffusion in directions respectively parallel to and at right angles to the direction of the magnetic field and it is assumed that the molecules of the solute consist of rotation ellipsoids, the ratio of the axes of the molecules may be calculated. Experiments made with *p*-azoxyphenetole as solvent gave for the conductivity ratio κ_0/κ_{90} , a mean value of 1.284 for diatomic molecules, such as hydrogen chloride, a mean of 1.44 for various hydroxy-derivatives of benzene, and of 1.59 for a number of naphthol derivatives. It is calculated that the axial ratio of the benzene molecules is 1.63 and that of the naphthalene molecules 2.93. If the minor axes are of the same length it can be shown that the relative lengths of the major axes should be as 1:1.79, which agrees with the ratio 1.63:2.93.

⁵⁰ H. Freundlich and H. Schucht, *Zeitsch. physikal. Chem.*, 1913, **85**, 660; *A.*, 1914, ii, 39; H. Freundlich and E. Hase, *ibid.*, 1915, **89**, 417; *A.*, ii, 317.

⁵¹ T. Svedberg, *Arkiv Kem. Min. Geol.*, 1913, **4**, Nr. 39; *A.*, 1914, ii, 97; *ibid.*, 1914, **5**, Nr. 11; *A.*, ii, 628. *Jahrb. Radioaktiv. Elektronik*, 1915, **12**, 129; *A.*, ii, 508.

The Hydrate Problem.

In recent years the problem of ionic hydration has received much attention. If the motion of the ions in an electric field is accompanied by the transference of water from one electrode to the other, it follows that the relative mobilities of the ions calculated from the observed changes of concentration at anode or cathode cannot represent the true values.

A new method⁵² of calculating the relative size of the water envelope has been suggested, which depends on the assumption that the motion of the ions conforms to the requirements of Stokes's formula. The radius R of any ion is thereby obtained in terms of the radius of the hydrogen ion which is supposed to have no water envelope. If r is the radius of the ion according to atomic volume data, then $R - r$ is found to be approximately equal to the diameter of a molecule of water. In other words, if r_w is the radius of a water molecule, then for a large number of univalent ions $R - r/2r_w$ is approximately equal to unity. The interpretation given to this result is that these ions are surrounded by a single layer of closely packed water molecules. Bivalent ions and some univalent ions give values for $R - r/2r_w$ greater than unity, indicating a greater degree of hydration than that represented by a single layer of close-packed water molecules. The number of water molecules thus found to be associated with various univalent ions is given in the following summary: H^+ 0, Cs^+ 13, Rb^+ 14, K^+ 16, NH_4^+ 17, Na^+ < 66, Li^+ < 120, Tl^+ 16, Ag^+ 29, Cl^+ 16, Br^+ 15, I^+ 15, ClO_3^+ 26, ClO_4^+ 17, NO_3^+ 19, CNS^+ 25.

The same author has also developed a new experimental method⁵³ for the determination of the ionic transport of water, which depends on the direct measurement of the changes in volume of the anode and cathode solutions. To this end, the middle portion of the solutions is made stationary by gelatinisation, and changes in volume are read off on capillary tubes which communicate directly with the anode and cathode chambers. A correction is applied for the effect of electro-endosmose, which is assumed to be independent of the concentration of the salt solution. The relative hydration numbers calculated from the changes in volume are found to be in close agreement with those obtained by Washburn,⁵⁴ who employed an entirely different method, involving the use of a non-transportable reference substance for the measurement of the ionic transfer of water. This is seen from the following table, in

⁵² H. Remy, *Zeitsch. physikal. Chem.*, 1915, **89**, 467; *A.*, ii, 310.

⁵³ H. Remy, *ibid.*, 529; *A.*, ii, 310.

⁵⁴ *Technology Quart.*, 1908, **211**, 386; *A.*, 1908, ii, 1009.

which the two values recorded under each ion are based on the assumption that the water envelope of the chlorine ion contains 6 or 10 water molecules respectively:

	Cl'.	Br'.	K'.	Na'.	Li'.	Ba''.	Ca''.
Remy	6(10)	5.0(9.2)	7.4(11.6)	11.9(18.4)	16.3(27.1)	2.3(17.0)	9.4(28.1)
Washburn..	6(10)	—	7.4(11.5)	11.6(18.0)	18.5(27.6)	—	—

According to experiments⁵⁵ with caesium chloride by the reference substance method, the Cs' ion is the least hydrated of the alkali metal ions.

In the investigation of the hydration of non-electrolytes electrical methods are inapplicable, but other observations, such as the influence of dissolved substances on the solvent power of water, are frequently considered to afford evidence of hydration and to provide a basis for its evaluation. This method has been applied in connexion with some recent determinations⁵⁶ of the change in the ratio of distribution of certain relatively inert substances, namely, ethyl acetate, phenol, and acetone between benzene (or petroleum) and water, which is brought about by the presence of sucrose or the alkali chlorides in the aqueous layer. In all cases the relative lowering of the solvent power per gram molecule of solute increases with diminution in the concentration of the sucrose or alkali salt. The value of this factor is not quite independent of the nature of the reference substance, as it ought to be according to the underlying theory, but this may probably be explained by the fact that the reference substances used are not chemically inert. The results for sucrose show an increase in the molecular hydration from 6.5 to 11 with increasing dilution. For sodium chloride the hydration changes from 9.5 in 4*N*- to 17.8 in 0.5*N*-solution. The corresponding numbers for potassium chloride are 8.6 and 16.4. For most dissolved substances the values of the equivalent relative lowering are greater than those obtained by previous authors from observations on the influence of dissolved salts on the solubility of gases in water. This suggests^{56a} that the specific character of the reference substance has less influence on the results than is the case in much of the previous work on the subject.

Transport Numbers and Potential Differences in Non-aqueous Media.

Transport measurements have shown that, for most ions, the relative mobilities are the same in ethyl alcohol as in water. The

⁵⁵ E. W. Washburn and E. B. Millard, *J. Amer. Chem. Soc.*, 1915, **37**, 694; *A.*, ii, 311.

⁵⁶ J. C. Philip and A. Bramley, *T.*, 1915, **107**, 377; *A.*, ii, 236.

^{56a} J. C. Philip and A. Bramley, *ibid.*, 1831.

hydrogen ion is, however, exceptional, in that transport data for alcoholic solutions of hydrogen chloride give $0.69/0.31=2.2$ for the ratio of the mobilities of the hydrogen and chlorine ions, whereas the data for aqueous solutions give $0.84/0.16=5.2$. These numbers suggest that, in general, the ions have approximately the same affinity for alcohol as for water, but that the hydrogen ion has a considerably greater affinity for the former solvent.⁵⁷

Measurements by the capillary electrometer method of the absolute potentials of mercury in contact with saturated aqueous and ethyl-alcoholic solutions of sodium chloride have shown that the values are identical (0.483 volt at 25°).⁵⁸ From the fact that the relative ionic mobilities are the same in the two solvents Lapworth infers that the absolute potential of mercury in a saturated solution of a salt in any solvent will be independent of the nature of the solvent provided that the cations and anions have the same affinity for the solvent. When the relative mobilities of cation and anion are different in two solvents, changes in the values of the single potential differences may be anticipated, and in agreement with this it is found that the potential of the hydrogen electrode falls from 0.299V in an alcoholic solution of 0.1N-hydrogen chloride to 0.186V in a corresponding aqueous solution.

Catalysis.

Recent work on acid catalysis has brought further evidence in support of the view that the catalytic effect represents the result of two simultaneous changes in which the active agents are the hydrogen ion and the non-ionised acid respectively.

Earlier observations on acid catalysed reactions in ethyl- and methyl-alcoholic solution were shown by Snethlage to admit of a satisfactory explanation on the basis of this theory. That the dual theory is applicable to reactions in aqueous solution has been confirmed in a remarkable way by experiments⁵⁹ on the catalytic influence of acids on the rate of isomeric change of acetone. For a series of five acids, covering a very considerable range of activity, the observed velocities of reaction are represented very satisfactorily by the equation $v = k_h c_h + k_m \cdot c_m$, in which k_h and k_m are coefficients representing the activity of the hydrogen ion and the non-ionised acid and c_h and c_m are the respective concentrations of these in the solution. The k_h values derived from the experiments with the five different acids, are identical within the limits of experimental error, whereas k_m

⁵⁷ A. Lapworth, *T.*, 1915, **107**, 857; *A.*, ii, 546.

⁵⁸ E. Newbery, *T.*, 1915, **107**, 852, 1520; *A.*, ii, 509, 816.

⁵⁹ H. M. Dawson and F. Powis, *T.*, 1913, **103**, 2135.

decreases rapidly with the strength of the acid, as shown by the following values of the activity ratio k_m/k_h : hydrochloric, 1.77; dichloroacetic, 0.50; $\alpha\beta$ -dibromopropionic, 0.152; monochloroacetic, 0.055; acetic, 0.0034.

Further support for the dual theory is afforded by new experiments⁶⁰ on the rate of hydrolysis of ethyl acetate in presence of various acids. The k_m/k_h values again show a rapid decrease with the acidity, the numbers obtained being: β -naphthalene-sulphonic, 0.98; trichlorobutyric, 0.55; hypophosphorous, 0.01; and cyanoacetic acid, 0.003. Variation of temperature is said⁶¹ to have but little influence on the value of the activity ratio.

An empirical attempt⁶² to correlate the activity ratio and the ionisation constant of the acid shows that the former is approximately proportional to the square root of the latter. On the other hand, if it is assumed that the action of the catalyst involves the formation of complexes between the acid and one or other of the reacting substances, then, according to Lapworth,⁶³ the ratio k_m/k_h is equal to $K_a \times k_1/k_2 K_s$, where K_a is the ionisation constant of the acid, K_s that of the salt-like complex of the acid with the reactive component, and k_1 and k_2 are the velocity coefficients for the reactions in which the non-ionised complex and the complex hydron respectively are concerned. According to this view, the activity ratio is not independent of the reaction by which the acidity is measured.

The success attending the dual theory in its application to recent work on acid catalysis is somewhat remarkable in view of the results which were obtained by Arrhenius⁶⁴ in his well-known experiments on the inversion of sucrose under the catalytic influence of weak acids in presence of the corresponding salts. The changes in velocity produced by the addition of sodium acetate or formate to solutions of the corresponding acids were such as to furnish most convincing evidence in favour of the view that, apart from a small neutral salt action, the catalytic activity of an acid is determined by the concentration of the hydrogen ion in the acid solution. The simple hydrogen ion theory of acid catalysis rests very largely on the evidence afforded by these measurements.

If by the addition of gradually increasing quantities of a neutral salt to a given solution of a moderately weak acid, the hydrogen

⁶⁰ Miss E. Ramstedt, *Medd. K. Vetensk. Nobelinstitut*, 1915, 3, [7], 1-33; A., ii, 541.

⁶¹ H. S. Taylor, *J. Amer. Chem. Soc.*, 1915, 37, 551; A., ii, 248.

⁶² H. S. Taylor, *Zeitsch. Elektrochem.*, 1914, 20, 201; A., 1914, ii, 353.

⁶³ A. Lapworth, *T.*, 1915, 107, 857; A., ii, 546.

⁶⁴ *Zeitsch. physikal. Chem.*, 1890, 5, 1.

ion concentration is reduced to a negligibly small value, then, according to the dual theory, the velocity of the catalysed reaction should not approximate to zero, but to a lower limiting value corresponding with the activity of the acid in the non-ionised condition. This limiting velocity can be calculated if the activity ratio k_m/k_h is known.

The application of the dual theory in these circumstances has been submitted to investigation by experiments⁶⁵ on the isomeric change of acetone with monochloroacetic acid as catalyst. For a fixed concentration of acid and gradually increasing quantities of the sodium salt, the velocity was found to approximate to a lower limiting value as required by the dual theory, and in all cases the observed velocities agreed with those calculated from the equation for the dual action, when in this equation the values used for k_h and k_m were those derived from experiments with the pure acid. It is evident that there is a great discrepancy between these results and those obtained by Arrhenius. To what extent the divergence is attributable to the difference in the nature of the reaction can only be determined by further investigation.

According to measurements of the rate of decomposition of nitrosotriacetoneamine,^{65a} under the influence of alkali hydroxides, there is no evidence of any catalytic action of the non-ionised base. Any such action is entirely masked by other effects.

The idea that molecules become reactive only when the energy content attains a certain critical value (see p. 11) has been applied⁶⁶ in an ingenious manner to account for the phenomena of catalysis. There is undoubtedly a certain similarity between the effects produced by rise of temperature and by the addition of catalysts. It is suggested that catalysis is essentially a radiation phenomenon, and that infra-red radiation is emitted by the catalyst and absorbed by the molecules of one of the reacting substances. In consequence of this absorption of energy, the internal potential energy of a relatively small number of molecules will be raised to the critical value. The rate at which this transformation is brought about will be more or less proportional to the concentration of the catalyst. On the assumption that the active agent in acid catalysed reactions occurring in aqueous solutions is the hydrogen ion, it is calculated that the wave-length of the radiation emitted will lie between $1\ \mu$ and $10\ \mu$. Many substances, including water, show marked absorption in this region, and if

⁶⁵ H. M. Dawson and C. K. Reiman, *T.*, 1915, **107**, 1426; *A.*, ii, 830.

^{65a} F. E. Francis, F. H. Geake, and J. W. Roche, *ibid.*, 1651.

⁶⁶ A. Lambie and W. C. M. Lewis, *ibid.*, 1914, **105**, 2330; 1915, **107**, 233; *A.*, ii, 160.

the energy absorbed gives rise to active water molecules, the theory may possibly be applied generally to acid catalysed reactions in aqueous solution.

Whatever the outcome of the hypothesis, it would seem necessary to abandon the idea of a mass-action equilibrium between active and inactive molecules, if temperature and catalytic effects are to be explained on a common basis.

A recent review of the phenomena of acid catalysis in particular and of the behaviour of electrolytes in general has led to the opinion that these are incompatible with the Arrhenius theory of ionisation. An alternative theory is put forward,⁶⁷ according to which the molecules of dissolved electrolytes are all undissociated, but a distinction is drawn between "active" and relatively inactive or "pre-active" molecules. A state of equilibrium exists between the two types of molecules. Solutions of salts, strong acids, and bases contain only active molecules, whereas solutions of weak acids and bases contain both kinds, the proportion of active molecules increasing with the dilution of the solution in accordance with the ordinary dilution law. The ratio Λ/Λ_{∞} has no simple significance, in that Λ represents the conductance due partly to "active" and partly to "pre-active" molecules, and Λ_{∞} the conductance of the molecules when all are in the "active" condition. It is claimed that the chemical, electrical, optical, thermal, and other properties of solutions of electrolytes can be interpreted in terms of this hypothesis. The claim is by no means substantiated by the evidence, and, in particular, the obvious difficulty presented by the dilution law is entirely unexplained. The validity of this relation for weak electrolytes is apparently irreconcilable with the assumption that each "active" molecule is formed from a single "pre-active" molecule.

The Valency Volume Theory.

The apparent success attained by the theory of Barlow and Pope in the correlation of crystalline form and chemical structure has undoubtedly provided much support for the view that valency is merely the expression of a simple geometrical property of close-packed assemblages of spheres. In the writer's experience, the fundamental ideas underlying the theory are not generally appreciated, and attention may accordingly be directed to a valuable paper by Barker,⁶⁸ in which these conceptions and the methods

⁶⁷ H. C. S. Snethlage, *Zeitsch. physikal. Chem.*, 1915, **90**, 1, 139; *A.*, ii, 615, 825.

⁶⁸ T. V. Barker, *T.*, 1915, **107**, 744; *A.*, ii, 546.

employed in the crystallographic applications of the theory are subjected to a searching criticism.

It is pointed out that strict adherence to the view that crystal edifices necessarily correspond with close-packed sphere assemblages involves an arbitrary selection from various possible structures. As yet, no proof has been given that close-packed assemblages are relatively stable as compared with other assemblages, and the considerations advanced by Pope and Barlow merely indicate a preference for a particular principle, for which they offer no justification.

An analysis of the methods which have been employed by the adherents of the theory in subjecting it to the test of experiment by reference to crystallographic data, shows that not only is the ambiguity which necessarily attaches to the choice of axial ratios made use of with the utmost freedom, but that where the desired correspondence between theory and observation is not immediately obvious, there is no hesitation in modifying arbitrarily the axial ratios by taking fractions or multiples of the axial lengths on the basis of an *ad hoc* process of trial. At least 90 per cent. of the available material is affected by this process. The vast possibilities of such arithmetical treatment are shown by calculation of the number of sets of axial ratios which are available for comparison with a "standard" set when these fractions and multiples are limited to those sanctioned by the usage of the Barlow-Pope school. In the rhombic system the number of possible variants is 2166, in the monoclinic 722, whilst in a comparison of rhombic with monoclinic substances the latitude is represented by 2166. Actual experience has shown that this number of variants affords, as a rule, several different ways of reproducing the numerical resemblances within the limits of ± 4 per cent., which may be regarded as the latitude allowed by most crystallographers. By reference to concrete examples it is shown that any desired numerical coincidence can be proved by exist for any given substance if the methods of Barlow and Pope are followed.

In the course of a critical discussion of the methods which may be legitimately employed in correlating geometrical form and crystal structure the Bravais principle⁶⁹ is again advocated as a means of determining the characteristics of the space-lattice system. For the identification of corresponding directions in the crystal, geometrical methods are inapplicable, and recourse must be had to such evidence as is afforded by cleavage directions and by the investigation of the effect of a crystal on the orientation of crystals of another substance which is deposited on its surface from solution.

⁶⁹ Compare *Ann. Report*, 1913, 245.

As already mentioned, 90 per cent. of the material advanced in support of the valency volume theory is considered irrelevant, and in the residue there are only some five substances in which the geometrical evidence is treated in accordance with objective methods of criticism. The analysis of the available material thus leads to the conclusion that the valency volume theory has so far received no general crystallographic support.

Electric Discharge through Hydrogen.

In two of last year's Reports considerable space was devoted to a review of experiments in which the effect of the passage of an electric discharge through pure hydrogen had been examined. The writer of the Report on Inorganic Chemistry⁷⁰ considered that a good case had been made out for the production of helium and neon under the influence of the discharge, and drew the conclusion that the experiments of Collie and Patterson afford evidence of atomic transformation. On the other hand, in the Report on Radioactivity⁷¹ the opinion was expressed that the balance of evidence appears to be against the theory that the inert gases are transmutational products, and that it is not yet proved that the positive results have any real significance. In the circumstances no apology is required for the inclusion in this section of a brief reference to the further work on the subject.

The results of this further investigation⁷² are in complete agreement with those obtained by R. J. Strutt⁷³ and T. R. Merton,⁷⁴ in that they afford no evidence of the formation of inert elements by the passage of the discharge through pure hydrogen. In these experiments the author has had the advantage of the experience of the earlier observers, not only in the design of the apparatus and in the methods employed for the detection of traces of the inert gases, but also in connexion with the possible influence of the type of discharge. Baly has suggested that success in these experiments may only be attainable if the discharge is "in tune" with the apparatus. It is therefore important to note that very special attention was paid by the author to variations in the conditions of discharge.

As the result of numerous experiments in which electric discharge was passed with three coils of different size, three different types of interrupter, through tubes of various shapes and sizes with palladium, platinum, and aluminium electrodes of varying size

⁷⁰ *Ann. Report*, 1914, 41.

⁷¹ *Ibid.*, 289.

⁷² A. C. G. Egerton, *Proc. Roy. Soc.*, 1915, [A], 91, 180; *A.*, ii, 132.

⁷³ *Proc. Roy. Soc.*, 1914, [A], 89, 499; *A.*, 1914, ii, 201.

⁷⁴ *Ibid.*, 90, 549; *A.*, 1914, ii, 726.

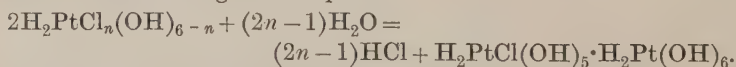
and shape, the analysis of the residual gas being carried out in various ways, it has been found that no change takes place in the gas as the result of electrical discharge. Contrary to the experience of Collie and Patterson, no helium or neon was found.

In face of all the available experimental evidence there appear to be no adequate grounds to warrant the interpretation of the results obtained by Collie and Patterson in favour of the theory of transmutation. Theoretical reasoning also leads to this conclusion, for Egerton has shown that if the maximum rate of formation is calculated on the assumption that the helium is produced (1) by a collision of four hydrogen atoms, (2) by the action of an electron on two colliding hydrogen molecules, values are obtained which are incomparably smaller than the rates observed by Collie and Patterson.

If, in spite of all the negative evidence, we admit the possibility that these authors' observations are of real significance, it does not seem unreasonable to ask that the reality should be substantiated by an explanation of the negative results generally obtained and by the formulation of the precise conditions under which positive results may be anticipated.

Photochemical Reactions.

The relation between the velocity of photochemical change, the incident and absorbed radiation, and its frequency forms the subject of a most interesting paper,⁷⁵ which might not inappropriately be described as furnishing a model for further work on photochemical change. The actual reactions investigated were the hydrolytic changes occurring in aqueous solutions of the chloroplatinic acids, which on exposure to ultraviolet light decompose in accordance with the general equation:



For light of given frequency the velocity is proportional to the quantity absorbed. It increases with the frequency of the incident radiation according to an exponential formula, and, contrary to what has been observed for many photochemical changes, it increases considerably with rise of temperature. The chief results are summarised by the equation:

$$v = \phi M e^{\alpha \nu} I_0 c (1 - e^{-\chi I_0 c})^\chi$$

in which ϕ and α are constants which depend on the photochemical sensitiveness, M is the molecular weight of the active substance, and χ the molecular absorption. By means of these constants the

⁷⁵ M. Boll, *Ann. Physique*, 1914, [ix], 2, 5, 226; A., ii, 122.

velocity v is represented as a function of the concentration c , the thickness of the absorbing layer l , the intensity I_0 , and the frequency ν of the incident radiation.

Apropos of an elaborate investigation of the action of ultra-violet light on water and dilute solutions of hydrogen peroxide, Tian⁷⁶ considers that the proportionality between the velocity of a photochemical reaction and the quantity of energy absorbed is only to be expected when the photochemical activity and the absorption of the active radiation vary with the concentration according to the same law. In the case of a unimolecular reaction, this condition is satisfied if absorption occurs in accordance with Beer's law. This does not seem to fit in with the observations on the decomposition of the chloroplatinic acids, for whilst Beer's law regulates the absorption, the reaction is bimolecular, and yet the results show that the velocity is proportional to the absorbed monochromatic radiation.

A year or two ago a general theory of photochemical change was developed⁷⁷ in which it was assumed that the first effect of the absorption of radiant energy is the production of free electrons and positively charged residues. Each molecule ionised in this way absorbs one quantum of energy or a small integral number of quanta. The photoelectric charge is then followed either by the interaction of the positive ions with unchanged molecules (primary light reactions) or by combination of the free electrons with neutral molecules, whereby these are rendered chemically active (secondary light reactions).

This theory has been tested by experiments in which solutions of the chloroplatinic acids (see above) were subjected to the action of ionising agents with the object of increasing the concentration of the ions and electrons. No appreciable change was, however, produced in the velocity of the photochemical reaction. Furthermore, the experiments with tetrachloroplatinic acid show that the ratio $\epsilon/h\nu$, where ϵ is the number of energy quanta absorbed in the decomposition of one molecule, ν the frequency of the incident rays, and h is Planck's constant, increases continuously from 0.2 for light of wave-length λ 2378 to 250 for λ 5460.

Whatever significance is to be attached to Bodenstein's theory and classification, it is evidently not applicable to the reactions investigated by Boll. At the same time, it must be admitted that the observed relations cannot legitimately be used as an argument against the law of photochemical equivalence, for the conditions

⁷⁶ A. Tian, "Thesis"; *A.*, ii, 828.

⁷⁷ M. Bodenstein, *Ber. Deut. physikal. Ges.*, 1913, 15, 690; *A.*, 1913, ii, 819.

stipulated in the derivation of this law are not fulfilled by the reactions in question.

In view of the extensive use of the Uviol-glass mercury arc lamp, attention may be directed to some recent measurements⁷⁸ of the distribution of the energy in the radiation from this source of light. The intensity of the ultraviolet, green, and yellow light relative to the blue is found to be much weaker for the Uviol than for the quartz mercury lamp. Application of the distribution data to observations on the oxidation of quinine by chromic acid⁷⁹ shows that illumination with light of different frequencies gives rise to velocities which are approximately in the ratio of the several intensities. In agreement with the conclusion deduced by Bruner,⁸⁰ the frequency of the existing radiation appears to have no appreciable influence on the velocity of the reaction, which is determined solely by the total quantity of energy absorbed. This conclusion is supported by earlier observations on the bleaching of organic dyes.⁸¹ It is, however, quite inconsistent with the relations exhibited by the hydrolysis of the chloroplatinic acids, and the discrepancy points to a fundamental difference in the character of the photochemical reactions in question.

If we admit the assumption that the primary change in a photochemical reaction is a photoelectric effect⁸² resulting in the ionisation and activation of the reacting components, the course of the reaction will obviously be dependent on the relative velocities of the photoelectric and chemical changes and on the reversibility or non-reversibility of the primary reaction.

H. M. DAWSON.

⁷⁸ A. J. Allmand, *T.*, 1915, **107**, 682; *A.*, ii, 400.

⁷⁹ R. Luther and G. S. Forbes, *J. Amer. Chem. Soc.*, 1909, **31**, 770; *A.*, 1909, ii, 632.

⁸⁰ *Zeitsch. Elektrochem.*, 1913, **19** 555; *A.*, 1913, ii, 745.

⁸¹ P. P. Lazareff, *Ann. Physik*, 1907, [iv], **24**, 681; *A.*, 1908, ii, 4.

⁸² Compare G. S. Landsberg, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 908; *A.*, ii, 718; A. V. Nazarov, *ibid.*, 1915, **47**, 943; *A.*, ii, 754.

INORGANIC CHEMISTRY.

THE year's work cannot be said to contain any outstanding investigation such as characterised that of 1914. On the other hand, in spite of the fewer number of papers published, the record of work is one of considerable interest to the inorganic chemist. It would perhaps be invidious to make special reference to any particular investigation, for such cannot but largely be a question of the personal element.

Atomic Weights.

In its Annual Report the International Committee has adopted changes in the atomic weight of the elements carbon, helium, lead, lutecium, praseodymium, radium, sulphur, tin, uranium, ytterbium, and yttrium. In the case of helium (4.00), radium (226.0), and ytterbium (173.5) the new values were mentioned in last year's Report on Inorganic Chemistry. The work leading to the new values for the remaining elements may be briefly described as follows:

Carbon.—The new value of 12.005 that has been adopted for carbon is based on the neutralisation of pure fused sodium carbonate with hydrobromic acid.¹ The relation between hydrobromic acid and silver was separately determined.

Lead.—Lead bromide was analysed by dissolving the pure fused salt in dilute acetic acid and then quantitatively treating it with a solution of silver nitrate, the silver bromide also being weighed. The value of 207.19 was obtained for the atomic weight. A similar method with lead chloride gave the value of 207.21.^{2,3} The mean value of 207.20 has been adopted by the Committee.

In connexion with the recent work on the isotopes of lead it may be mentioned that in the above work eleven specimens of lead salts were obtained from non-radioactive sources, but no evidence of any dissimilarity was found.

¹ T. W. Richards and C. R. Hoover, *J. Amer. Chem. Soc.*, 1915, **37**, 95; *A.*, ii, 96.

² G. P. Baxter and T. Thorwaldson, *ibid.*, 1020; *A.*, ii, 455.

³ G. P. Baxter and F. L. Grover, *ibid.*, 1027; *A.*, ii, 456.

Some further work has appeared on the atomic weight of lead of radioactive origin.⁴ Twenty kilograms of purest selected Joachimsthal pitch-blende were extracted with pure reagents, and the lead thus obtained had an atomic weight of 206.405. A crystalline uranium ore from an old primary geological formation in Morogoro, German East Africa, gave lead with an atomic weight of 206.046, whilst bröggerite from Moos, Norway, gave 206.063. The arc and spark spectrum of common lead and lead with an atomic weight of 206.046 showed absolute identity. This identity between the spectra of common lead and lead from radioactive sources has independently been confirmed between the limits $\lambda=3500$ and $\lambda=4100$.⁵ An accurate investigation of the spectrum line with a wave-length of $\lambda=4058$ with a Fabry and Perot étalon made with both types of lead showed that if there be any difference in the wave-length of the lines in the two cases, such difference must be less than 0.003 Ångstrom.

Praseodymium.—Pure praseodymium chloride was prepared in the following way⁶: Ten kilograms of praseodymium ammonium nitrate containing much lanthanum and cerium salts were submitted to a prolonged fractional crystallisation from dilute nitric acid. The pure salt was then converted into oxalate and then ignited to the oxide. The oxide was dissolved in nitric acid and again precipitated as oxalate and then again ignited to oxide. The oxide was then dissolved in hydrochloric acid and the chloride three or four times recrystallised by passing hydrogen chloride into the concentrated solution at 0°. The atomic weight by precipitation with silver nitrate was found to be 140.92. The value of 140.9 has been adopted by the International Committee.

Sulphur.—The molecular weight of sodium sulphate was determined by conversion of pure sodium carbonate into sodium sulphate, the molecular weight of sodium carbonate having been previously determined.⁷ The atomic weight of sulphur was found to be 32.06, taking carbon as 12.005.

Uranium.—Uranium bromide was prepared by heating a mixture of uranium oxide and carbon in bromine vapour. The atomic weight of uranium was determined from the ratio $\text{UBr}_4:\text{AgBr}$, and was found to be 238.175.⁸ The International Committee has adopted the value 238.2.

⁴ O. Hönigschmid and Mlle. S. Horovitz, *Monatsh.*, 1915, **36**, 355; *A.*, ii, 635.

⁵ T. R. Merton, *Proc. Roy. Soc.*, 1915, [A], **91**, 198; *A.*, ii, 119.

⁶ G. P. Baxter and O. J. Stewart, *J. Amer. Chem. Soc.*, 1915, **37**, 516; *A.*, ii, 263. ⁷ T. W. Richards and C. R. Hoover, *ibid.*, 108; *A.*, ii, 96.

⁸ O. Hönigschmid, *Zeitsch. Elektrochem.*, 1914, **20**, 452; *Compt. rend.*, 1914, 158, 2004; *A.*, 1914, ii, 662.

Tin. Stannic chloride was prepared by direct union of its elements and purified by fractional distillation.⁹ A portion of the final fraction of this purified material was further fractionated twice and collected in weighed bulbs in a sealed and exhausted apparatus. The solutions for analysis were prepared by breaking the bulbs in dilute nitric acid containing either oxalic acid or tartaric acid, and were then treated with a slight deficit of silver nitrate. The slight deficit of silver was made up by the addition of a measured volume of a dilute standard silver solution. The progress of the titration and the attainment of the end-point were ascertained by nephelometric measurements. Fifteen distinct fractions of stannic chloride were analysed, and the atomic weight of tin was found to be 118.70.

Lutecium.—Ytterbium was fractionally separated into ytterbium (neoytterbium) and lutecium.¹⁰ The atomic weight of both elements was determined by conversion of the oxalate into the oxide, and that of lutecium was found to be 175.0, a value which has been adopted by the International Committee.

Yttrium.—The atomic weight of yttrium was determined by the conversion of yttrium sulphate, dehydrated at 400°, to the oxide at high temperature. The mean of six determinations gave the atomic weight of 88.75.¹¹ The mean of all experiments, including some previous determinations,¹² is 88.7, which has been adopted by the International Committee.

Tantalum.—The determinations of the atomic weight of tantalum up to the present have not given satisfactory agreements, and a new determination has been made from the ratios $2\text{TaCl}_5:\text{Ta}_2\text{O}_5$ and $\text{TaCl}_5:5\text{Ag}$. The results of the latter ratio gave values of the atomic weight between 180.90 and 181.36.¹³ The silver chloride was precipitated in the presence of 5.5 per cent. hydrofluoric acid. In view of the somewhat large divergences between the atomic-weight values the investigation is to be continued.

Cadmium.—It was found that cadmium can be purified by the recrystallisation of cadmium bromide. The method adopted for the determination of the atomic weight was the electrolysis of cadmium chloride solutions using a mercury cathode, and the value of 112.417

⁹ H. V. A. Briscoe, *T.*, 1915, **107**, 63.

¹⁰ C. A. von Welsbach, *Monatsh.*, 1913, **34**, 1713; *A.*, 1914, ii, 130.

¹¹ R. J. Meyer and M. Weinheber, *Ber.*, 1913, **46**, 2672; *A.*, 1913, ii, 962.

¹² R. J. Meyer and T. Wuorinen, *Zeitsch. anorg. Chem.*, 1913, **80**, 7; *A.* 1913, ii, 323.

¹³ G. W. Sears and C. W. Balke, *J. Amer. Chem. Soc.*, 1915, **37**, 833; *A.* ii, 351.

was found.¹⁴ This is distinctly higher than the International value, and is confirmed by the electrolysis of cadmium bromide solutions, but the investigation is being continued. This result has been criticised by Hulett and Quinn,¹⁵ and therefore the matter is still *sub judice*.

Molybdenum.—Pure molybdenum was prepared by the reduction of MoO_3 in a stream of pure hydrogen. The atomic weight was determined by conversion of molybdenum into the trioxide by heating it in a current of air and oxygen, the value obtained being 96.029.¹⁶

Columbium.—Sodium metacolumbate, $\text{Na}_2\text{O}, \text{Cb}_2\text{O}_5, 7\text{H}_2\text{O}$, was prepared and then dehydrated at 800° . The anhydrous salt was heated in a current of sulphur chloride vapour, when it was converted into sodium chloride. As a mean of seven determinations the atomic weight was found to be 93.13.¹⁷

Molecular Weights.

The application of Avogadro's law, which is valid for saturated vapours, to the determinations of the volume, pressure, and temperature corresponding with a given weight of water vapour shows that the molecular weight is 18.016 only at 32° .¹⁸ As the temperature rises above 32° the molecular weight continuously increases, due to the formation of H_4O_2 , at 270° the percentage of association being 41.41. At temperatures below 32° the molecular weight diminishes owing to spontaneous ionic dissociation of the water vapour. It is found that these phenomena are functions of the concentration and depend on Le Chatelier's law of mobile equilibrium.

The general opinion that the vapours of the ammonium haloid salts are entirely dissociated refers only to the unsaturated vapours, for some experiments on the saturated vapours have shown that this dissociation is not by any means complete.¹⁹ The method employed was that of the static isoteniscope.²⁰ It was found that ammonium chloride vapour between 280° and 330° is dissociated to the extent of 67—63 per cent., the degree of dissociation decreases

¹⁴ G. P. Baxter and N. L. Hartmann, *J. Amer. Chem. Soc.*, 1915, **37**, 113; *A.*, ii, 98.

¹⁵ G. A. Hulett and E. L. Quinn, *ibid.*, 2046; *A.*, ii, 782.

¹⁶ J. H. Müller, *ibid.*, 2046; *A.*, ii, 782.

¹⁷ E. F. Smith and W. K. van Haagen, *ibid.*, 1783; *A.*, ii, 692.

¹⁸ G. Oddo, *Gazzetta*, 1915, **45**, i, 319; *A.*, ii, 683.

¹⁹ A. Smith and R. H. Lombard, *J. Amer. Chem. Soc.*, 1915, **37**, 38; *A.*, ii, 86.

²⁰ A. Smith and A. W. C. Menzies, *ibid.*, 1910, **32**, 1412, 1434; *A.*, 1910, ii, 1036, 1037.

ing slightly between these two temperatures. In the case of ammonium bromide at 320° the vapour is dissociated to the amount of 39 per cent., and at high temperatures the percentage dissociation decreases linearly to 10 per cent. at 388°. Ammonium iodide vapour, on the other hand, is associated, especially at low temperatures, but as the temperature rises the amount of association decreases. The last result is confirmed in a later paper, in which are also given the densities of the saturated vapour of phosphorus pentachloride between 90° and 160°. ²¹ The saturated vapour is somewhat dissociated at 90°, and there is approximately a constant amount of 4 per cent. dissociation between 110° and 160°. The latent heat of evaporation of the pentachloride is 15,500 calories per molecule.

Specific Heats.

Certain determinations of specific heats have been made during 1915 of which mention may be made. That of platinum at high temperatures has been determined by measuring the changes in the temperature of an incandescent platinum filament caused by the sudden suppression of a definite small resistance in the circuit. ²² The values obtained were as follows:

<i>t</i> °.	<i>C_v</i> .	<i>C_p</i> .
980	1.118	1.206
1178	1.116	1.273
1353	1.187	1.309
1440	1.213	1.344
1543	1.240	1.382

The values of *C_v* were calculated from those of *C_p* by the Nernst and Lindemann formula, which for platinum is:

$$C_p = C_v [1 + 63 \times 10^{-6} (T + 273)].$$

It is interesting to note that the specific heat rises with increase of temperature, even at high temperatures, which is contrary to what would be expected.

Reference was made in the report of 1913 to the determination by Dewar of the specific heats of the elements at very low temperatures. Further data are now available as regards the specific heats of copper and lead. The method adopted was as follows: A measured quantity of heat was developed within a block of the metal and the increase of temperature noted, the whole operation being carried out in a liquid hydrogen thermostat. The following values for their atomic heats were obtained ²³:

²¹ A. Smith and R. H. Lombard, *J. Amer. Chem. Soc.*, 1915, **37**, 2055; *A.*, ii, 767.

²² L. Fabaro, *Nuovo Cim.*, 1915, [vi], **9**, i, 123; *A.*, ii, 672.

²³ W. H. Keesom and H. K. Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 894; *A.*, ii, 83.

Lead.		Copper.	
Atomic heat.	<i>t.</i> abs.	Atomic heat.	<i>t.</i> abs.
1.56	14.19°	0.05	15.24°
2.98	22.31	0.14	21.505
5.04	46.25		
5.67	40.86		

The general results agree with those calculated from Debye's formula.

Some determinations of the specific heat of ice of varying degrees of purity are worthy of record.²⁴ From experiments with four samples of ice it was found that the specific heat, *s*, in 20° calories at any temperature *θ* is given by $s = 0.5057 + 0.001863\theta - 79.751/\theta^2$, where 1 is the difference between 0° and the initial freezing temperature of the water from which the ice was obtained. From this it may be seen that the specific heat of pure ice is given by $s = 0.5057 + 0.001863\theta$. The latent heat of fusion of ice in 20° calories was found to be 79.76.

In the report for 1913 reference was made to some measurements of the specific heat of helium and various diatomic gases, and the increase in the ratio of the two specific heats obtained at the boiling point of liquid air. Recently a somewhat similar increase in the ratio of the two specific heats of certain gases, due to the effect of increase of pressure, has been published.²⁵ The gases investigated were air, carbon dioxide, sulphur dioxide, ammonia, and ethylene. The measurements were made by Behn and Geiger's modification of Kundt's method,²⁶ taking into account the deviations from the gas laws. The ratio of the two specific heats increases in all cases with increase of pressure, and the increment increases with the magnitude of the deviation of the compressibilities from those required by Boyle's law. The following values may be quoted:

	<i>C_p/C_v</i> .	Pressure.
Air	1.404	0.5 Atmosphere.
	1.411	3.5
CO ₂	1.288	0.5
	1.307	3.67
SO ₂	1.273	0.5
	1.347	2.5
NH ₃	1.297	0.5
	1.410	3.5
C ₂ H ₄	1.275	0.5
	1.334	3.67

²⁴ H. C. Dickinson and N. S. Osborne, *J. Washington Acad. Sci.*, 1915, 5, 338; *A.*, ii, 412.

²⁵ K. Scholer, *Ann. Physik*, 1914, [iv], 45, 913; *A.*, ii, 220.

²⁶ *Ber. Deut. physikal. Ges.*, 1907, 5, 657; *A.*, 1908, ii, 99.

Electric Discharge.

In last year's Report some prominence was given to the controversy between Strutt on the one hand and Tiede and Domcke on the other as regards the formation of active nitrogen. Whereas the former maintained that the presence of oxygen was unnecessary in the production of the active gas, the latter experimenters concluded that they had proved that traces of oxygen were absolutely necessary. A somewhat unsatisfactory conclusion was published in a joint paper under the names of H. B. Baker and the three authors mentioned above. It was stated that the contradictory results were largely due to the difference in the apparatus used, and it was considered probable that the production of active nitrogen is favoured by traces of oxygen, although in a suitable apparatus the result can be obtained even with the purest nitrogen. The writer pointed out, however, that no real explanation was given in this paper of the non-production of active nitrogen by Tiede and Domcke, except possibly the somewhat unsatisfactory reference to differences in the apparatus. This unsatisfactory conclusion was fully recognised by Strutt himself, who deals with the question in a further paper.²⁷ After Tiede and Domcke's visit to this country Strutt still felt convinced that although nitrogen could be prepared which gave an increased glow when oxygen was added to it, yet nitrogen containing less than 0.001 per cent. of oxygen gives a very decided glow, this nitrogen being prepared by treating commercial nitrogen for a long time with cold phosphorus. Some further experiments, however, have now shown that it is possible to prepare nitrogen which gives very little glow by exposing commercial nitrogen for some hours to the action of the liquid alloy of sodium and potassium at 300°. The reduction of the glow is very noticeable after the alloy has been heated several times with successive fillings of the nitrogen. The addition of oxygen at once restores the glow, the maximum effect being observed when the concentration of oxygen is about 1/750 of the whole.

An extended series of experiments has proved the fact that many other gases act as catalysts in the formation of the glow. Methane, ethylene, acetylene, carbon monoxide, carbon dioxide, sulphur dioxide, hydrogen sulphide, chlorine, and water and mercury vapours all cause a restoration of the glow, the most active being hydrogen sulphide. The general conclusion thus is arrived at that for the optimum formation of the afterglow a catalyst must be present, and that this need not be oxygen. The explanation of the

²⁷ (Hon.) R. J. Strutt, *Proc. Roy. Soc.*, 1915, [A], **91**, 303; *A.*, ii, 336.

formation of the glow as being due to an oxidising effect, in the opinion of Strutt, thus falls to the ground.

Now that the controversy has reached the present stage outside criticism is admissible, and the writer would point out that twenty years ago he convinced himself that it was quite possible to obtain a specimen of nitrogen which, at any rate in an ordinary vacuum tube, shows no trace of afterglow. This occurrence of the afterglow is familiar enough to anyone who has worked on the spectra of the permanent gases, although its explanation was discovered relatively recently by Strutt. In criticising the most recent work on the subject, the effect of the catalysts may be considered, and the conclusion seems inevitably to follow that really pure nitrogen would give no glow at all, even in Strutt's apparatus. The method of purification of the nitrogen would seem at once to be cumbersome and unsatisfactory. In actual fact, the preparation of the liquid alloy of sodium and potassium free from hydrocarbons is a matter of extreme difficulty. The catalytic effect of three hydrocarbons has already been discovered, and hence it is advisable rigidly to guard against the presence of any hydrocarbons. In some experiments on the thermal expansion of hydrogen under diminished pressure, the hydrogen was prepared from its compound with sodium.²⁸ Hydrogen under atmospheric pressure was bubbled through liquid sodium in a glass vessel until the sodium had absorbed as much of the gas as possible. The temperature was then raised and the pressure reduced, when pure hydrogen was evolved. It was then found necessary to repeat the operation several times in order to obtain the hydrogen free from hydrocarbons.

Again, the complete absence of oxygen from the nitrogen does not seem to have been clearly established. It may savour of hypercriticism, but it may be questioned whether the liquid alloy is as good an absorbent for oxygen as might at first thought be imagined. The first action of the alloy would be to dry the nitrogen and oxygen mixture absolutely, and then the fact that sodium may be distilled unchanged in pure, dry oxygen comes to the front. The easiest way to prepare small quantities of pure, dry nitrogen is to use the method described by Ramsay and Travers in their work on the rare gases,²⁹ namely, to place a small pellet of phosphorus in a fairly strong tube full of mercury and inverted over mercury. The top of the tube is warmed with a Bunsen flame

²⁸ E. C. C. Baly and (Sir) W. Ramsay, *Phil. Mag.*, 1894, [v], **38**, 301; *A.*, 1895, ii, 38.

²⁹ (Sir) W. Ramsay and M. W. Travers, *Proc. Roy. Soc.*, 1901, **67**, 329; *A*, 1901, ii, 237.

until the pellet of phosphorus melts. Air, previously freed from carbon dioxide, is then driven into the tube by a capillary. The phosphorus inflames at once, care being taken to admit the air sufficiently rapidly to cause vigorous combustion. Nitrogen so made does not seem to give any glow whatever.

Further, no evidence is forthcoming in Strutt's paper that any one of the catalysts he used was free from contamination by oxygen. For example, the preparation of carbon monoxide free from admixture with oxygen is exceedingly difficult, the only test for the absence of oxygen being that it gives the Swan spectrum when examined at low pressure.

Again, the evidence afforded by the oxygen containing catalysts is indecisive, since all four, carbon monoxide, carbon dioxide, sulphur dioxide, and water vapour tend to decompose into their elements when subjected under diminished pressure to the electric discharge. The one possible exception is mercury vapour, which does seem of itself alone able to restore the glow in nitrogen. It must not be forgotten, however, that mercury always contains considerable amounts of oxides dissolved in it, and the removal of these is abnormally difficult. Even when the mercury has been distilled in a vacuum it is still contaminated, as may be seen at once when it is shaken with pure water in a stoppered bottle. Possibly these oxides may have been decomposed completely in the repeated heating which Strutt applied, although this is questionable.

Finally, Strutt's claim that pure nitrogen can be prepared by the action of cold phosphorus on commercial nitrogen is not very sound. Ozone and low oxides of phosphorus are always formed, and the latter are by no means easily removed. Their presence in the nitrogen when the discharge is passed might produce sufficient oxygen to give rise to the glow.

Some further results on the production of helium and neon in vacuum tubes during the passage of the electrical discharge may be noted.³⁰ The work of Collie, Patterson, and Masson was fully dealt with in last year's Report. The new results are entirely negative. The electric discharge was passed with three different size coils, three different types of interrupters, through various sized and shaped tubes with palladium, platinum, and aluminium electrodes of various shapes and sizes. The analyses of the residual gases were carried out by phosphorus and charcoal in various ways, but no change of the gases, such as the production of helium or neon, was detected.

A theoretical discussion shows that it would seem to be impossible

³⁰ A. C. G. Egerton, *Proc. Roy. Soc.*, 1915, [A], **91**, 180; *A.*, ii, 132.

for helium to be produced by the association of hydrogen atoms or molecules together. First of all, the probability is dealt with that helium can be produced by a fourfold collision of hydrogen atoms, and it is shown that there would have to be at least 7.7×10^8 such collisions per second in order to produce a detectable quantity of helium in ten hours. In the second place, the possibility that the helium might be produced by the collision of a cathode particle with two molecules of hydrogen, and it is shown that the probability is that only one helium atom would be produced in about 10^{11} years. On the other hand, it would seem possible that the helium may be formed by the disintegration of the metallic electrodes or of the oxygen, silica, and other constituents of the glass or gases in the discharge tube.

Allotropy.

In the section of last year's Report dealing with this subject reference was made to the fact that copper, cadmium, and zinc had been added to the list of metals which exhibit allotropy. The work in this field has during this year considerably been extended. Further experiments on bismuth³¹ have shown that the transition temperature between the α - and β -modifications of this metal, at first considered to be 75° , depends on the previous history of the metal.³² Finely divided bismuth which has been in contact with a 10 per cent. solution of potassium chloride for twelve hours diminishes in volume at 70° , whereas the same sample of the metal before treatment shows an increase in volume between 75° and 100° .

Again, it seems that lead exhibits allotropy.³³ Pure lead, containing not more than 0.001 per cent. of copper and 0.0006 per cent. of iron, has D_4^{25} 11.3299. After immersion for some days in a 40 per cent. solution of lead acetate containing 100 c.c. of nitric acid (D 1.16) in a litre, the lead undergoes a marked change in appearance. No gas is evolved and the metal contracts, so that it is obvious that the change is a physical one. The density of the changed lead as obtained at 15° , 25° , and 50° is found to be 11.3415, 11.3283, and 11.3129 respectively. These results would seem to prove the existence of several allotropic modifications of lead. The change in the physical characteristics of the lead in

³¹ E. Cohen, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1236; *A.*, ii, 471.

³² E. Cohen and A. L. T. Moesveld, *Chem. Weekblad*, 1913, **10**, 656; *A.*, 1913, ii, 779.

³³ E. Cohen and W. D. Helderman, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 822; *A.*, ii, 52; *Zeitsch. physikal. Chem.*, 1915, **89**, 733; *A.*, ii, 457.

lead acetate solution has independently been observed,³⁴ as has also the change of lead when kept in lead nitrate and lead chloride solutions. The change does not occur in acetic acid, nitric acid, or sodium acetate solutions, and therefore is due to the presence of lead ions.

Further, the metals antimony, potassium, and sodium have also been found to exhibit allotropy. In the case of antimony, the ordinary form consists of two modifications with a transition temperature very near 101°. If, however, the dilatometer containing the powdered metal is heated for fifty minutes at 150° before examination at 96°, a diminution in volume at this temperature is observed, followed by a steady increase in volume. It is concluded that at 96° three allotropic modifications are present in antimony.³⁵

Potassium consists of two modifications with a transition temperature of 59.6—59.8°, the ordinary form being a metastable mixture of both modifications.³⁶

Sodium also exists in two modifications, the β -form being less dense than the α -form.^{37, 38} The change $\beta \rightarrow \alpha$ takes place most rapidly at about 95°. Since under the same conditions liquid sodium is formed more rapidly from the β -form than from the α -form, it appears that the change $\beta \rightarrow \alpha$ is exothermic.³⁹

Some further work may also be recorded on the allotropy of sulphur.⁴⁰ The preparation and properties of the modification S_π were described in the Report for 1913, and now there must be added a fourth modification, S_ϕ . Concentrated hydrochloric acid at 0° is added to a cold solution of sodium thiosulphate, and the aqueous solution is then shaken with toluene. After a short time S_ϕ separates from the toluene as orange-yellow crystals. There is little doubt that S_λ , S_μ , S_ϕ , and S_π represent four different molecular complexes with definite and distinct properties. It is believed that S_λ is S_8 , S_ϕ is S_6 , and that S_π is S_4 . The solutions of S_ϕ are less strongly coloured than those of S_π , and the difference between the two forms is definitely proved by their solubili-

³⁴ H. Heller, *Zeitsch. physikal. Chem.*, 1915, **89**, 761; *A.*, ii, 674.

³⁵ E. Cohen and J. C. van den Bosch, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 645; *A.*, ii, 58; *Zeitsch. physikal. Chem.*, 1915, **89**, 757; *A.*, ii, 471.

³⁶ E. Cohen and S. Wolff, *Proc. K. Akad. Amsterdam*, 1915, **17**, 1115; *A.*, ii, 258.

³⁷ E. Cohen and G. de Bruin, *ibid.*, 1915, **17**, 926; *A.*, ii, 83.

³⁸ E. Cohen and S. Wolff, *ibid.*, 1915, **18**, 91; *A.*, ii, 634.

³⁹ For a general account of Professor Cohen's work see E. Cohen and W. D. Helderman, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1238; *A.*, ii, 417; and E. Cohen, *Trans. Faraday Soc.*, 1915, **10**, 216; *A.*, ii, 565.

⁴⁰ A. H. W. Aten, *Zeitsch. physikal. Chem.*, 1914, **88**, 321; *A.*, ii, 254.

ties. Some difficulty was found in the experimental work owing to the existence of two forms of S_μ , the ordinary insoluble form and an unstable liquid form which is soluble. The difficulty lay in proving that a solution of S_π or S_ϕ is not a solution of S_μ . It may be stated, however, that the experimental evidence is clearly in favour of S_π and S_ϕ and S_μ being three separate and distinct modifications of sulphur.

It may perhaps be mentioned here that a new crystalline variety of silver has been prepared.⁴¹ Spongy silver is first made by igniting in a crucible pure and dry precipitated silver tartrate. Nitric acid (D 1.42), from which the lower oxides of nitrogen have been removed by boiling with carbamide, is allowed to act on the spongy silver at the ordinary temperature. At first some action takes place, with the formation of silver nitrate and nitrous acid, but after a time the solution of silver ceases, and on allowing the mixture to remain, with occasional shaking, for about a fortnight, the remaining silver is converted into long, needle-shaped crystals. This is considered to be a new variety of crystalline silver belonging to the cubical system.

Valency.

In the Annual Report for 1913 a brief account was given of the work carried out by Ephraim on the ammine derivatives of bivalent metals, the object of this series of investigations being to compare the secondary valencies of the metals in these compounds. Since the publication of that report this work has been carried considerably further, especially in connexion with the secondary valencies of the central atoms in complex anions. In order to compare the stability of complex anions with that of complex cations, a considerable number of acid chlorides of organic bases having the general formula $M[Cl(HCl)]$ were prepared, and the dissociation pressure of the hydrogen chloride at various temperatures was determined.⁴² It was found that the dissociation temperature for a given pressure varies very little for the majority of acid salts of the tertiary amines. The relation between the atomic volume and the secondary valency of the bivalent metals has further been investigated by a study of the ammines of the chlorates, bromates, and iodates of the metals.⁴³ It was found, however, that in the two former series of compounds the dissociation curves are limited by the explosive nature of the compounds. In the case of the iodates, the dissociation occurs at relatively low

⁴¹ T. C. Choudhri, *J. Amer. Chem. Soc.*, 1915, **37**, 2037; *A.*, ii, 768.

⁴² F. Ephraim, *Ber.*, 1914, **47**, 1828; *A.*, 1914, i, 827.

⁴³ F. Ephraim and A. Jahnsen, *ibid.*, 1915, **48**, 41; *A.*, ii, 166.

temperatures. It seems definitely found once more that the constant product $\sqrt[3]{v} \cdot \sqrt[5]{T}$, where v is the atomic volume and T the absolute dissociation temperature for a given pressure, is slightly high for nickel and decidedly so for cadmium. It is probable that these discrepancies are due to an alteration in the atomic volume when the combination with ammonia takes place, and it may be pointed out that this view is supported by a comparison of the molecular volumes of the compounds.

In general, it is found that those factors which increase the stability of the molecules with complex cations, notably the smallness of the central atoms, work in exactly the opposite direction in the case of complex anions.⁴⁴ Thus the salts of complex metallohexammine cations decrease in stability with the atomic volume of the metal, whilst the hydroxides, carbonates, nitrates, sulphates, and peroxides of the alkaline earth metals, $M[O(H_2O)]$, $M[O(CO_2)]$, $M[O(N_2O_5)]$, $M[O(SO_3)]$, $M[O(O)]$, increase in stability. The effect of the atomic volume of the central atom in the cation is very definite, but that of the atomic volume of the central atom in the anion is doubtful. It follows from this that the stability of the ammines, $M(NH_3)_nX_2$, depends not only upon the metal, but also on the central atom of the anion.⁴⁵ The influence of these two oppose one another. The stability of the molecule as a whole, therefore, is the result of two influences, and consequently there may be found no direct parallelism between analogous compounds. For example, the hexammine and pentammine series of nickel and zinc with the same acid radicles are not analogous to one another. An independent measurement of the affinity for ammonia in the hexammines of nickel and cobalt has shown that this increases in the order chloride, bromide, iodide,⁴⁶ but in the case of the monoammines it would seem that the reverse is the case.

Group I.

Some measurements of the physical constants of hydrogen and the halogen hydrides have been made. The density of liquid hydrogen, determined by the displacement method, was found to be 0.07105 at -252.83° and 745.52 mm.⁴⁷ In the case of the halogen hydrides, the following values were found for the melting points and boiling points: hydrogen chloride, m. p. -111.4° , b. p.

⁴⁴ F. Ephraim, *Ber.*, 1915, **48**, 624; *A.*, ii, 441.

⁴⁵ F. Ephraim and E. Boller, *ibid.*, 638; *A.*, ii, 454.

⁴⁶ W. Biltz and B. Felkenhauer, *Zeitsch. anorg. Chem.*, 1914, **89**, 134; *A.*, ii, 466.

⁴⁷ H. Augustin, *Ann. Physik*, 1915, [iv], **46**, 419; *A.*, ii, 117.

—83.4°; hydrogen bromide, m. p. —88.1°, b. p. —67.1°; hydrogen iodide, m. p. —50.9°, b. p. —35.5°. ⁴⁸

Mention may also be made of the melting points of the metals lithium, sodium, and potassium, which have been redetermined with great accuracy, and are now recorded as 180.1°, 97.6°, and 62.04° respectively. ⁴⁹

In connexion with the alkali metals, careful search has been made for an alkali element of higher atomic weight than caesium. ⁵⁰ Rather more than 3.5 kilos. of caesium nitrate was prepared from pollucite, and the whole of this was subjected to a prolonged fractional crystallisation, since it seemed likely from the solubilities of the nitrates of the alkali metals that the nitrate of any alkali metal of higher atomic weight than caesium would be the least soluble of all. After eighteen series of crystallisations, the least soluble fraction, which contained about 3 grams of caesium nitrate, was carefully examined. The spectrum of this fraction showed no difference from that of one of the intermediate fractions, nor did this least soluble fraction show any sign of radioactivity.

Finally, the atomic weight of the metal in the least soluble fraction was determined by the analysis of the chloride. The average result of the determinations gave the value 132.82, which agrees closely with that adopted by the International Committee, namely, 132.81. It is clear that these experiments give no indication of the existence of an unknown alkali element.

Reference was made in the Report for 1912 to the preparation of a chemically active form of hydrogen by heating metallic filaments of tungsten, palladium, or platinum to high temperatures in hydrogen at very low pressures. ⁵¹ The hydrogen appears to dissolve in the metals as atoms, and these atoms diffuse out and have little opportunity of joining together again to form molecules. The losses of heat from tungsten wires have been measured in hydrogen at pressures from 0.01 mm. up to ordinary atmospheric pressure, ⁵² and the results of these experiments have now been applied to the calculation of the degree of dissociation and the heat of formation of molecular hydrogen. ⁵³ A large amount of chemical evidence has also been accumulated. If hydrogen at low pressures comes into contact with metallic wires at temperatures above 1300° abs., part of the hydrogen is converted into an active

⁴⁸ O. Maas and D. McIntosh, *Trans. Roy. Soc., Canada*, 1914, [iii], 8, 65; *A.*, ii, 314.

⁴⁹ A. Bernini and C. Cantoni, *Nuovo Cim.*, 1914, [vi], 8, ii, 241; *A.*, ii, 82.

⁵⁰ G. P. Baxter, *J. Amer. Chem. Soc.*, 1915, 37, 286; *A.*, ii, 97.

⁵¹ I. Langmuir, *ibid.*, 1912, 34, 1310; *A.*, 1912, ii, 1162.

⁵² I. Langmuir and G. M. J. Mackay, *ibid.*, 1914, 36, 1708; *A.*, 1914, ii, 717.

⁵³ I. Langmuir, *ibid.*, 1915, 37, 417; *A.*, ii, 249.

modification which remains adsorbed on glass surfaces for long periods of time. This active hydrogen can react at room temperature with oxygen or with many reducible substances, or can dissolve in metals such as platinum. There are good reasons for thinking that this active hydrogen is hydrogen in the atomic condition. A new series of experiments was made in order to measure more accurately than before the heat losses from a tungsten wire at temperatures from 800° to 3500° abs. and at pressures of hydrogen ranging from 0.01 mm. up to atmospheric pressure. Similar experiments were made with nitrogen.

At temperatures below that at which dissociation occurs the heat loss from the wires decreases steadily as the pressure is decreased. Only at pressures above 200 mm. do convection currents play any important part. The normal heat conductivity is easily separated from the abnormal effect due to dissociation of the hydrogen. With nitrogen there is no abnormal increase in the heat loss at high temperatures.

The dissociation of the hydrogen does not occur in the space around the wire, nor by the impact of molecules against its surface, but takes place only among the hydrogen molecules which have been absorbed (dissolved?) by the metal of the wire. Within the metal the reaction occurs so rapidly that equilibrium may be assumed to prevail at all times. The equilibrium constant within the metal may, however, be very different from that in the gas phase.

It is assumed that there is no "adsorption film" on the surface of the wire through which the hydrogen has to diffuse, but that the absorption takes place by the collision of the molecules (or atoms) against the surface of the wire. A certain proportion of the molecules striking the surface may be reflected without absorption. Thus, of all the hydrogen molecules striking against the surface, it may be assumed that a certain fraction a_2 is absorbed, whilst the fraction $1-a_2$ is reflected. Similarly, of all the hydrogen atoms striking the surface, the fraction a_1 is absorbed.

In general, the partial pressures of atomic hydrogen in the gas immediately surrounding the wire will not be that corresponding with the equilibrium at the temperature of the wire. The partial pressure of atomic hydrogen immediately around the wire depends on, first, the rate at which atomic hydrogen escapes from the wire; secondly, the rate at which atomic hydrogen is absorbed by the wire; and thirdly, the rate at which it can diffuse away from the wire.

It has been found possible by thermodynamical reasoning to develop a quantitative theory by which the dissociation constant

K (in the gas phase) may be calculated in terms of W the heat carried from the filament by dissociation, q the heat of reaction, D the diffusion-coefficient, and the two coefficients a_1 and a_2 . The resulting general equation is of the form:

$$K = [(W/q)^2(P/D + 1/a_1)^2] / [P - (W/q)(P/D + 1/a_2)],$$

where P is the total pressure. By comparing this equation with the experimental data, it is found possible so to choose the quantities K , q , D , a_1 , and a_2 that the resulting equation agrees excellently with the experiments at all temperatures and pressures. At the same time the values of K conform to the thermodynamical requirement given by van't Hoff's equation, $dl nK/dT = q/RT^2$.

The values of the quantities K , q , D , a_1 , and a_2 which were used in these calculations, and found to give the best agreement between experiment and theory, are as follows:

Dissociation Constant K .—The dissociation constant is defined by the equation $K = p_1^2/p_2$, p_1 and p_2 being the partial pressures (in mm.) of atomic and molecular hydrogen respectively. It is found that $\log_{10} K = 7.77 - 19700/T$, whence it is calculated that the degree of dissociation at 760 mm. is 0.0033 at 2000°, 0.014 at 2300°, 0.031 at 2500°, 0.17 at 3100°, and 0.34 at 3500° abs.

Heat of Formation of Hydrogen Molecules.—By applying van't Hoff's equation it is found that the heat of reaction for 2 grams of hydrogen is 84,000 calories at constant volume and 90,000 calories at constant pressure.

Diffusion-coefficient of Atomic Hydrogen in Molecular Hydrogen.—This quantity is found to be $D = 2.14 \cdot 10^{-3} T$. This result is 4.2 times greater than that found previously (*loc. cit.*) by calculation from the principles of the kinetic theory. This difference suggests that the hydrogen molecules are more or less "transparent" to hydrogen atoms. The effect is probably quite analogous to that of the abnormal mobility of the hydrogen and hydroxyl ions in aqueous solutions.

The Coefficients a_1 and a_2 .—The coefficient a_1 is found to be constant and equal to unity, whilst a_2 is apparently constant and equal to 0.68. In other words, all the hydrogen atoms striking the filament are absorbed by it, and 68 per cent. of all the hydrogen molecules are absorbed. The velocity of the reaction is thus determined, practically entirely, by the equilibrium conditions within the wire.

The rate at which hydrogen at very low pressures is dissociated by a tungsten wire at 1200—1500° has been calculated, and found to be eight to ten times greater than the greatest observed rate at which active hydrogen is deposited on glass surfaces. In view of the marked fatigue effects characteristic of this adsorption of active

hydrogen by glass, the agreement is close enough to lend further support to the theory. The quantitative evidence of the dissociation of hydrogen may therefore be said to extend over a temperature range from 1200° to 3500° abs., in which the degree of dissociation increases in the ratio 1:70000.

Experiments from the heat losses from tungsten wires in mixtures of nitrogen and hydrogen also yield results in accord with the theory. The diffusion-coefficient of hydrogen atoms through nitrogen is found to be $D = 2.5(T/273)$, which is in excellent agreement with the value calculated from the kinetic theory.

It is a well known fact that the addition of sulphuric acid in sufficient quantity to the saturated solution of a hydrated salt with which the acid does not react, will cause the salt to crystallise, either as a lower hydrate or in the anhydrous condition. It is possible in certain cases to use this means of preparing lower hydrates in order to determine all the stable hydrates which a normal sulphate can form at a given temperature. The method has been applied to the determination of the hydrates of copper sulphate at 25° , and the results have been plotted as a curve showing the range of conditions under which each of the three hydrates, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, is formed.⁵⁴ The conditions for the trihydrate are very narrow; the pentahydrate has the widest range, being stable in contact with solutions containing as much as 49 per cent. of sulphuric acid.

Very few cuprous salts of oxygen acids are known, and it is sometimes erroneously stated that such compounds do not exist. Two new cuprous salts have been prepared, namely, cuprous oxalate⁵⁵ and cuprous carbonate.⁵⁶ The best known member of this class of compounds is red cuprous sulphite, $\text{Cu}_2\text{SO}_3 \cdot \text{H}_2\text{O}$. A concentrated solution of sodium hydrogen sulphite is added to a solution of cupric sulphate, the slight precipitate is filtered off, and the filtrate is gently warmed. Sulphur dioxide is evolved and the red salt crystallises out. This is sprinkled little by little into a hot solution of an excess of oxalic acid. Much sulphur dioxide is evolved and the colour of the solid changes from bright red to brown. The precipitate is collected, washed with water, and finally with alcohol. Analysis shows that the salt is cuprous oxalate, $\text{Cu}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. When the salt is heated at about 95° for two hours the colour changes to dark grey. When heated alone in a crucible the substance changes to grey and then to greenish-grey, giving off traces of water, and finally undergoes violent

⁵⁴ L. C. Daniels, *J. Amer. Chem. Soc.*, 1915, **37**, 1167; *A.*, i, 493.

⁵⁵ P. Carles, *Bull. Soc. chim.*, 1915, [iv], **17**, 163; *A.*, ii, 459.

⁵⁶ H. W. Foote, *J. Amer. Chem. Soc.*, 1915, **37**, 288; *A.*, ii, 97.

decomposition. The grey substance has the same composition as the original brown compound.

When metallic copper is exposed to the action of air and liquid ammonia it becomes coated after a time with copper carbonate and the action ceases. When the copper thus coated is left in contact with the ammonia the blue colour of the surface changes to green and then slowly to reddish-yellow, which is permanent. The material may be detached by boiling water, and is cuprous carbonate produced by the reducing action of the copper.

Mention may also be made of two new sodium borates containing more boron trioxide than ordinary borax, namely, $\text{Na}_2\text{O}, 3\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}, 4\text{B}_2\text{O}_3$, which melt at 694° and 783° respectively, whilst ordinary borax melts at 730° .⁵⁷

Group II.

A new determination has been made of the critical temperature of mercury. The mercury was heated in sealed quartz tubes, and the changes in the volume of liquid and vapour phases observed up to 1400° .⁵⁸ In order to obtain the density of the saturated vapour at high temperatures, similar tubes were heated, and the temperature at which the liquid just disappeared was determined. From the data obtained it was found that the critical temperature must be lower than 1650° . It is, however, higher than 1500° , for in one experiment the temperature was raised to this value and liquid mercury was still present.

Some investigations have been made of the effect of small proportions of salts of certain organic bases and also of gelatin on the electrolytic deposition of zinc from a solution containing zinc and ammonium sulphates, a pure zinc anode and a brass cathode being used.⁵⁹ When very small amounts of these substances are present and when the current density is low, a homogeneous, uniform, fine-grain deposit is obtained, but if either the proportion of the added compound or the current density is increased the zinc then separates irregularly in nodular masses. It is invariably noticed that the first uniform deposit only dissolves slowly in hydrochloric acid. It is suggested that the organic substance present in the neighbourhood of the cathode is absorbed by the metallic granules which separate initially in a state of high dispersion, and so renders the deposit fine-grained. At a later stage the organic compound tends to coat the cathode with a more or less impermeable varnish, and

⁵⁷ J. Bonomarev, *Zeitsch. anorg. Chem.*, 1914, **89**, 383; *A.*, ii, 449.

⁵⁸ J. Bender, *Physikal. Zeitsch.*, 1915, **16**, 246; *A.*, ii, 673.

⁵⁹ A. Mazzucchelli, *Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 503, 626; *A.*, ii, 670, 671.

thus induces passivity. At certain points of the cathode which are accidentally favoured, deposition may continue at an increased current density, the crystalline, nodular masses being thus formed. So far as they have progressed, the experiments indicate that the cathodic deposition of the zinc is influenced more than the anodic dissolution.

Some interest attaches to an investigation of the displacement by zinc of certain metals from solutions of their salts.⁶⁰ In the case of copper salts a zinc plate, attached by means of wax to a glass stirrer, was kept in continual motion in a solution of copper sulphate of definite initial concentration, and the alteration in the latter was determined at regular intervals by titration with $N/100$ -sodium thiosulphate solution. Experiments were made with $N/100$ - and $N/20$ -copper sulphate solution at the ordinary temperature and at 25° , the surface of the zinc being polished in every case. The results obtained show that the velocity-constant of the reaction increases during the first half hour, but that there is no sharply defined period of induction. The reaction follows the equation of the first degree, as is required by the theory of diffusion, so that its velocity is proportional to the first power of the concentration of the copper sulphate.

In order to determine the lapse of time between the immersion of the zinc and the commencement of the deposition at its surface of the other metal, some further experiments have been made with solutions of copper sulphate and of nickel and cobalt chlorides, sulphates, and nitrates. The zinc cylinders used were coated with wax, except over one end-surface, which was polished and arranged uppermost in the liquid in order to admit of examination under a lens. Zinc reacts with copper salts far more readily than with those of nickel and cobalt, and in solutions of chlorides the action begins decidedly earlier than in solutions of the corresponding sulphates. With nickel and cobalt nitrates no action occurs, although in a concentrated solution of the former a precipitate of the hydroxide gradually appears. In solutions of copper sulphate the reaction does not give rise to the liberation of gas, but in nickel chloride and sulphate solutions the deposition of the metal is followed some time later, and in cobalt chloride, very considerably later, by the evolution of gas bubbles. The gas is probably hydrogen, resulting from the decomposition of the water by the zinc-nickel or zinc-cobalt couple. The deposition of the metal is not influenced by the presence of NO_3 ions, and two equivalent solutions containing (1) nickel sulphate and potassium

⁶⁰ M. Centnerszwer and J. Drukker, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 528; *A.*, ii, 563.

nitrate, and (2) nickel nitrate and potassium sulphate gave identical results.

It is concluded that a period of induction exists, not only in the displacement of hydrogen, but also in that of metals by zinc. In the latter case, however, this period of induction is far shorter than in the former, and is noticeable only with very dilute solutions of the salts. The retardation, therefore, of the dissolution of zinc in acids during its initial period must be due to the difficulty with which the hydrogen ions are converted into gaseous hydrogen, and to the resistance offered by the dielectric layer formed by the discharge of the hydrogen ions at the surface of the electrode.

In the displacement of metals by zinc, "local elements" are formed very shortly after the initial deposition of the metal on the zinc, the velocity of the reaction being proportional to the sum of the currents of all these cells. Since the resistances of the latter are small, the electrochemical interchange of metals proceeds with great rapidity, and the velocity of the reaction is conditioned solely by the rate of diffusion of the dissolved salt from the solution to the surface of the zinc; in this phase, therefore, the reaction follows the theory of diffusion.

In the displacement of hydrogen by metals the bubbles of hydrogen pass away from the surface of the metal, and the cause of the establishment of local cells is thus absent. Such local galvanic elements may, however, be formed in this case (1) in consequence of the presence of admixed metals, and (2) owing to solution of hydrogen in the zinc. Since both of these causes act very slowly, the period of induction is greatly prolonged in this case.

Some work may be recorded on the peroxides of the alkaline earth metals and of zinc.⁶¹ When hydrogen peroxide is added to barium hydroxide solution the octahydrate, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, is always obtained when more than one molecule of barium hydroxide is present per molecule of hydrogen dioxide. Above 60° it is formed, whatever the composition of the solution. The anhydrous peroxide cannot be obtained from aqueous solution. Below 40° the diperoxyhydrate, $\text{BaO}_2 \cdot 2\text{H}_2\text{O}_2$, is obtained from solutions containing much hydrogen peroxide. A compound, $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$, may also be obtained between 30° and 60° .

Anhydrous strontium peroxide is obtained from very concentrated solutions above 50° , otherwise the octahydrate is formed. The diperoxyhydrate is not obtained by direct precipitation, but only by the action of concentrated hydrogen peroxide on the octahydrate at low temperatures.

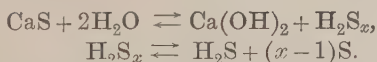
⁶¹ E. H. Riesenfeld and W. Nottebohm, *Zeitsch. anorg. Chem.*, 1914, **89**, 405; **90**, 150; *A.*, ii, 449, 454.

Calcium peroxide separates in the anhydrous form from very concentrated solutions near 0° , and above 40° even from very dilute solution. The octahydrate is obtained from dilute solutions at the ordinary temperature. A dihydrate may be prepared from the anhydrous compound. The diperoxyhydrate resembles that of strontium. By the action of water, all these compounds are slowly converted into the octahydrates.

If hydrogen peroxide is added to an ammoniacal solution of zinc nitrate at -5° , a white, amorphous precipitate is obtained which, after being dried, gives the ratio $\text{ZnO}:\text{active oxygen}:\text{water}=1:0\cdot84:0\cdot71$. If the powder is stirred with concentrated hydrogen peroxide, this ratio may be increased to $1:0\cdot91:0\cdot87$, which indicates the presence of zinc peroxide, ZnO_2 .

The lime-sulphur wash, which is used extensively as a fungicide, is prepared by boiling together one part of quicklime, two or more parts of sulphur, and ten parts of water.⁶² The concentrated commercial product generally contains the polysulphides, thiosulphate, sulphite, and sulphate of calcium, the polysulphides and the thio-sulphate preponderating. There is no doubt that much of the sulphur in the lime-sulphur solution is in a very loosely combined condition, for some early experiments showed that it was possible to extract it with sulphur solvents. Some objection arose to these experiments on account of the non-exclusion of oxygen and carbon dioxide.

Extraction of the fluid with sulphur solvents causes a continuous removal of free sulphur. This continuous formation of sulphur is due to the hydrolytic dissociation of the polysulphides, which accounts also for the strongly alkaline nature of the solution. Since also hydrogen sulphide is readily liberated in quantity when the liquid is heated, the formation of the sulphur is probably due to the following equilibria:



Attempts were made to detect the existence of a more stable polysulphide in solution by measuring the sulphur removed at stated intervals, and although, by themselves, the results cannot be regarded as conclusive, owing to experimental difficulties, yet it is significant that a lower rate of extraction sets in when the ratio between the polysulphide sulphur (S_p) plus monosulphide sulphur (S_m) and the monosulphide sulphur alone is between 1.6 and 2.3.

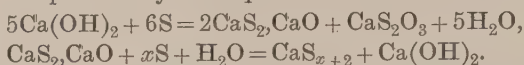
Attempts were made to prepare calcium disulphide by boiling together lime and sulphur in the calculated proportions, but in

⁶² S. J. M. Auld, *T.*, 1915, **107**, 480; *A.*, ii, 345.

every case Herschell's crystals were obtained. The analytical results show that the main product in these crystals corresponds with the formula $\text{CaO}, \text{CaS}_2, 7\text{H}_2\text{O}$.

It is concluded that in the absence of air, lime and sulphur react in aqueous solution, with the formation only of calcium polysulphides (or oxysulphides) and calcium thiosulphate. When an excess of sulphur is used, the ratio of $(S_m + S_p)/S_m$ usually lies between 4.5 and 5.0, but may exceed the latter figure under certain conditions.

The formation of the polysulphides from lime and sulphur may probably be expressed by the equations



By obtaining the redissolution of precipitated sulphur in the polysulphide solution, evidence was obtained indicating the possible existence of polysulphides at least as high as CaS_7 .

It is suggested that the polysulphides of calcium possess the constitution



the atoms of sulphur in the chain becoming progressively more loosely attached.

Group III.

In the last three reports accounts were given of the work carried out by Stock and his co-workers on the hydrides of boron, and the preparation and identification were described of the four compounds B_2H_6 , B_4H_{10} , B_6H_{12} , and $\text{B}_{10}\text{H}_{14}$. Some difficulty as regards the valency of boron towards hydrogen arises, since it would seem that it must be quadrivalent. An investigation therefore has been made into the action of the halogens on these compounds, more particularly on B_2H_6 , with the view of throwing some light on the question.⁶³

In the first place, some improvements were made in the preparation of the starting material, B_4H_{10} . The crude gas, prepared by the action of hydrochloric acid on the "magnesium boride," is first passed through a tube at -40° , whereby white crystals of $\text{B}_{10}\text{H}_{14}$, m.p. 99.5° , are collected. The gas is then passed through a large U-tube at -80° , and therein a little B_4H_{10} , some silicon hydride, and chiefly B_6H_{12} are condensed. Finally, the main bulk of the gas is condensed by cooling with liquid air. From 100 grams of the boride there were obtained 0.02 gram of $\text{B}_{10}\text{H}_{14}$ and 95 c.c. (0° and 760 mm.) of B_4H_{10} . The B_4H_{10} when heated at 100°

⁶³ A. Stock, E. Kuss, and O. Priess, *Ber.*, 1914, **47**, 3115; *A.*, ii, 340.

decomposes fairly rapidly, and the only gaseous products are hydrogen and B_2H_6 . The B_2H_6 from this process was condensed in a bath made by stirring liquid air into alcohol until the mass is almost solid. In this way a temperature of -125° to -115° may be maintained in a Dewar vessel for some hours.

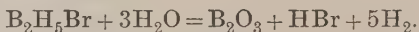
The density of B_2H_6 is found to be 13.97. The gas condenses in needles when cooled slowly, and at the ordinary temperature it is not attacked by oxygen to any extent after some days. It is decomposed, however, at once by traces of moisture, but it is not acted on by hydrogen sulphide even at 100° . If the liquid is suddenly exposed to air it inflames. The action of chlorine and bromine on the hydrides has been the subject of an exhaustive study. In the case of the solid hydride, B_4H_{10} , the reaction is very sluggish, and it is found that displacement of the hydrogen by the halogen takes place, and not addition. When the solid is left in a large excess of bromine for six months, the residue, after evaporation, gives on analysis a result agreeing with a formula between $B_{10}H_{12}Br_2$ and $B_{10}H_{11}Br_3$. Definite compounds seem to be isolated by fractional crystallisation from a mixture of benzene and light petroleum. The alkaline solutions of these compounds reduce permanganate solution, and then on acidifying yield B_4H_{10} . The acid solutions also reduce permanganate solution and slowly evolve B_4H_{10} , together with other as yet unknown boron compounds.

In the case of B_2H_6 , chlorine causes explosions at the ordinary temperature, whilst bromine reacts only very slowly even in the light. The reaction is, however, complete after a few hours at 100° . In every experiment it was found that half of the halogen used is returned as the halogen hydride, and thus it follows that the action is one of substitution and not addition. If the halogen is in excess, the unimolecular haloids BCl_3 and BBr_3 are formed, and not B_2Cl_6 and B_2Br_6 . Since this fact is of great importance, an investigation was made into the intermediate stages involved in the conversion of B_2H_6 into the unimolecular haloid. The reaction was studied with an insufficient quantity of halogen, and the explanation was found in the action of bromine. When B_2H_6 is treated with about one-third of the quantity of bromine necessary for the complete reaction, the intermediate compounds $B_2H_4Br_2$, etc., are not formed. The products obtained are almost exclusively the two extreme compounds B_2H_5Br and BBr_3 . The intermediate compounds, although initially formed in small amounts, readily undergo rearrangement into the two extreme compounds. Indeed, the monobromide, B_2H_5Br , itself decomposes into B_2H_6 after a short time. The formation of hydrogen bromide was never

observed, and no evidence could be obtained of the existence of BHBr_2 , BH_2Br , $\text{B}_2\text{H}_2\text{Br}_4$, B_2HBr_5 , or B_2Br_6 . The reaction with chlorine is similar, but the intermediate compounds and the monochloride, $\text{B}_2\text{H}_5\text{Cl}$, are far more volatile and labile than the corresponding bromine derivatives, and consequently the mechanism of the reaction was somewhat obscured.

It follows, therefore, that by the action of chlorine or bromine or an excess of B_2H_6 the derivatives $\text{B}_2\text{H}_4\text{X}_2$ and $\text{B}_2\text{H}_3\text{X}_3$ are first formed, and these rapidly decompose and rearrange themselves into $\text{B}_2\text{H}_5\text{X}$ and B_2H_6 on the one hand and BX_3 on the other.

The monochloride, $\text{B}_2\text{H}_5\text{Cl}$, is a spontaneously inflammable gas, whilst the monobromide, $\text{B}_2\text{H}_5\text{Br}$, is a colourless gas with an irritating odour. The monobromide melts at -104° , and the vapour pressure rises from 3 mm. at -80° to 335 mm. at -5° . The boiling point at 760 mm. is calculated to be 10° . It burns with a pale green flame, and fumes in the air owing to the reaction with water



It reacts immediately with potassium hydroxide, like B_2H_6 , to form the hypoborate, KOBH_3 . No appreciable reaction takes place when it is treated with sodium, and an attempt to convert it into B_4H_{10} failed.

It is clear from these results that boron must be quadrivalent, and hence the highest negative valency must be four. The highest positive valency is three, and hence it is evident that boron does not obey the Abegg and Bodländer rule that the sum of the two valencies is eight. Some substances have been described, notably BOCl_3 and B_2S_5 , in which the positive valency is supposed to be five, but the constitution of these is very questionable.

All attempts to prepare a hydride of boron with only one atom of boron in the molecule have failed. Boron trialkyls have been prepared, but they are as unsaturated as triphenylmethyl, whilst the corresponding hydrides, BH_3 and CH_3 , seem to be equally impossible of isolation.

Concomitantly with the above work, the properties of the two unimolecular haloids of boron, BCl_3 and BBr_3 , have been studied. The boron trichloride was prepared by the action of chlorine on Moissan's boron in a glass tube, the temperature being so regulated that the glass was attacked as little as possible.⁶⁴ The gas obtained was condensed at -80° and then shaken with mercury. It was freed from hydrogen chloride and silicon chloride by fractional distillation in a high vacuum from a bath at -78° . The

⁶⁴ A. Stock and O. Priess, *Ber.*, 1914, **47**, 3109; *A.*, ii, 339.

fractions were collected in a vessel cooled in liquid air, and the first and last fractions were rejected. The pure substance melts at -104° and boils at $13^{\circ}/764$ mm. The vapour density is 58.43 and the vapour pressure rises from 4 mm. at -80° to 753 mm. at 12.4° . The boiling point at 760 mm. is calculated to be 12.5° . The vapour reacts energetically with fat, and therefore a special valve was designed to eliminate the use of taps in the apparatus employed.

Boron trichloride does not attack hot mercury, nor does it combine with chlorine even at -80° .

Boron tribromide was prepared by passing bromine vapour over boron at a dull red heat.⁶⁵ The product was purified by shaking with mercury, and it was then fractionally distilled under atmospheric pressure. The compound is a liquid with m. p. -46° and b. p. $99.1^{\circ}/740$ mm. The molecular weight as found by the cryoscopic method in benzene is 252. Its vapour pressure rises from 0.7 mm. at -50° to 730 mm. at 90° . The vapour attacks fat as energetically as does that of the chloride.

The effect of electrolysing solutions of sodium and potassium borates with varying proportions of alkali hydroxide has been examined.⁶⁶ No perborate is formed even when the anode is thoroughly cooled, and even very concentrated solutions only yield a minute quantity. Perborates introduced into the anode compartment are destroyed owing to the formation of hydrogen peroxide.

Mention may be made of the preparation of pertetraboric acid and its salts. These, for example the sodium salt, $\text{Na}_2\text{B}_4\text{O}_{11}$, are prepared by the action of hydrogen peroxide, or a mixture with a metallic peroxide, on pyroboric acid, preferably at below 0° .⁶⁷

Group IV.

As was noted in the Report for 1912, Riesenfeld and Mau differentiated between the true percarbonates and the ordinary carbonates containing hydrogen peroxide of crystallisation. Some further work has been published dealing with compounds which seem to belong to the latter class.⁶⁸ The addition of hydrogen peroxide to the alkali metal carbonates causes the formation of compounds such as $\text{CsCO}_3 \cdot 2\text{H}_2\text{O}_2$, $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$. These substances exhibit the properties of per-

⁶⁵ A. Stock and E. Kuss, *Ber.*, 1914, **47**, 3113; *A.*, ii, 340.

⁶⁶ W. G. Polack, *Trans. Faraday Soc.*, 1915, **10**, 177; *A.*, ii, 557.

⁶⁷ J. Auer, D.R.-P. 281134, *J. Soc. Chem. Ind.*, 1915, **34**, 613; *A.*, ii, 557.

⁶⁸ P. V. Cazanecki, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1110; *A.*, ii, 332.

oxides, and decompose at the ordinary temperature with the evolution of carbon dioxide and the formation of the corresponding metal hydrogen carbonate as a result of the perhydrolysis of the carbonates. Magnesium carbonate and hydrogen peroxide in solution give a substance to which is assigned the formula $\text{MgO}_{2\frac{1}{5}}\text{MgCO}_3\cdot\text{H}_2\text{O}$, but it may be pointed out that it is more probable from analogy to the alkali metal compounds that the formula is $\text{MgO}_{\frac{1}{5}}\text{MgCO}_3\cdot\text{H}_2\text{O}_2$. All these salts react with titanous acid or chromic acid and sulphuric acid, and they yield ozone with concentrated sulphuric acid and chlorine with concentrated hydrochloric acid. Since with neutral potassium iodide they evolve iodine only slowly, these compounds conform to the test established by Riesenfeld and Mau for the carbonates containing hydrogen peroxide of crystallisation.

In the estimation of unsaturated hydrocarbons by treatment with bromine, some uncertainty arises if carbon monoxide is present in large amounts. This is due to the formation of carbonyl bromide, and the conditions under which it is formed have been investigated.⁶⁹ The extent to which the action proceeds in sunlight depends upon the proportion of water vapour that is present, and when the carbon monoxide and bromine have been carefully dried the velocity of reaction is very low. The reaction takes place in two stages, $\text{CO} + \text{Br}_2 = \text{COBr}_2$ and $\text{COBr}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HBr}$. In the first stage, equilibrium is reached with a small concentration of the carbonyl bromide, which must be removed as it is formed in order that the reaction may continue.

Some information has been obtained as to the nature of the changes which occur during the extraction of metallic lead from galena by the roasting process. The equilibrium conditions in the system lead-sulphur-oxygen have been investigated by the determination of the dissociation pressures between 500° and 800° and examination of the solid phases present under varying conditions of temperature and pressure.⁷⁰

When sulphur dioxide is removed from a mixture of lead sulphide and lead sulphate, five successive univariant systems with three solid phases can be recognised: (1) $\text{PbS-PbSO}_4\text{-PbO}$, PbSO_4 ; (2) Pb-PbS-PbO , PbSO_4 ; (3) Pb-PbO , $\text{PbSO}_4\text{-2PbO}$, PbSO_4 ; (4) Pb-2PbO , $\text{PbSO}_4\text{-3PbO}$, PbSO_4 ; (5) Pb-3PbO , $\text{PbSO}_4\text{-PbO}$.

From the vapour-pressure curve for the first system it is found that the thermal value of the reaction $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$ is $-99,543$ calories.

⁶⁹ A. Piva, *Gazzetta*, 1915, **45**, i, 219; *A.*, ii, 447.

⁷⁰ W. Reinders and F. Goudriaan, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 703; *A.*, ii, 47.

In the Report for 1913 reference was made to work on the production and properties of red lead. An investigation of the dissociation pressures of the higher oxides of lead may now be recorded.⁷¹ The oxide was heated at various temperatures, which were kept constant within 0.2 per cent. by an ingenious electrical device in connexion with a manometer, pump, and oxygen reservoir. Red lead, purified by repeated heating with lead nitrate or acetate solution, reaches equilibrium only very slowly when dissociating. The pressure-temperature curve between 445° and 607° is quite smooth, and there is no evidence of a solid solution of the monoxide, PbO , in red lead, Pb_3O_4 , or of any intermediate oxide. The monoxide thus prepared is yellow, with a green shade when obtained at high temperatures. The same pressures are obtained in the reverse process, namely, when oxygen is admitted to lead monoxide which has been prepared from the decomposition of red lead in a vacuum. The red modification of the monoxide prepared in the wet way only absorbs oxygen very slowly at 540°, and retains its colour. The reactivity varies with the mode of preparation.

The dissociation of lead peroxide gives unstable products down to $\text{PbO}_{1.36}$ at 361°. Red lead is not formed, but the products are solid solutions of varying compositions, unstable in regard to red lead. The limit is reached at $\text{PbO}_{1.36}$, beyond which litharge appears at a new phase. The formation of definite oxides, such as Pb_2O_3 , Pb_5O_7 , or Pb_5O_8 , has not been confirmed.

A systematic study has been made of the plumbichlorides, which are prepared by mixing solutions of the acid, H_2PbCl_6 , with solutions of the chlorides of the metals or bases.⁷² The compounds are anhydrous and have the general formula X_2PbCl_6 or $(\text{R}\cdot\text{NH}_3)_2\text{PbCl}_6$. In those cases where the crystalline system could be measured, regular and rhombic forms predominate. The compounds of the alkali metals and of derivatives of the pyridine and quinoline series are especially stable, whilst the aliphatic ammonium compounds tend to decompose in the air, the crystals becoming white and chlorine being evolved. Hydrogen peroxide exerts an immediate reducing action, plumbous chloride being separated and gas evolved. Concentrated ammonia solution yields a pale brown and a dilute solution an almost black precipitate containing lead dioxide.

Reference may also be made to two investigations of cerium compounds. A double potassium perceric carbonate was described

⁷¹ W. Reinders and L. Hamburger, *Zeitsch. anorg. Chem.*, 1914, **89**, 71; *A.*, ii, 457.

⁷² A. Gutbier and M. Wissmüller, *J. pr. Chem.*, 1914, [ii], **90**, 491; *A.*, i, 217.

by Job, and was given the formula $\text{Ce}_2\text{O}_3(\text{CO}_3)_3, 4\text{K}_2\text{CO}_3, 12\text{H}_2\text{O}$.⁷³ The salt was prepared by the interaction of cerium ammonium nitrate and hydrogen peroxide in a concentrated solution of potassium carbonate. The process has been modified as follows.⁷⁴ A saturated solution of potassium carbonate is treated with hydrogen peroxide, and then cerous ammonium nitrate is added. The mixture is heated rapidly to 60° , and kept at that temperature as long as the colour deepens. Carbon dioxide is then passed through the solution until no further potassium hydrogen carbonate is precipitated, and then the mixture is cooled to 0° until as much as possible of the potassium hydrogen carbonate has crystallised out, the passage of carbon dioxide being continued. The mixture is filtered through glass wool and left to remain at 5° . The crystals which separate are dried in the air, and on analysis are found to have the formula $\text{Ce}_2\text{O}_4(\text{CO}_3)_2, 4\text{K}_2\text{CO}_3, 12\text{H}_2\text{O}$. The salt readily loses its water of crystallisation, and then changes in colour from transparent ruby to opaque orange-yellow. It is found that of the available oxygen in the compound, two-thirds is to be regarded as peroxidic oxygen. Reference may also be made to the similar compound prepared by Baur, $\text{Ce}_2\text{O}_4(\text{CO}_3)_2, 4\text{K}_2\text{CO}_3, 10\text{H}_2\text{O}$.⁷⁵

An examination of the hydrolysis of cerium sulphate has been made, and on the basis of the phase rule a pale yellow, basic sulphate, $\text{CeO}_3, \text{SO}_3, 2\text{H}_2\text{O}$, has been isolated.⁷⁶ This salt is sparingly soluble in water, and is hydrolysed thereby, giving an acid solution. When sulphuric acid is added to concentrated solutions of ceric sulphate, it is probable that basic salts of a deep red colour are produced. When ceric sulphate, after being dried at 115° , is heated for thirty hours at 105° , it is converted into a white compound having the formula $3\text{CeO}_2, 4\text{SO}_3$. This substance appears to exist in two modifications, which are both hydrolysed by water, but yield differently coloured, insoluble residues.

When ceric sulphate or the compound $3\text{CeO}_2, 4\text{SO}_3$ is heated for a prolonged period at temperatures below red heat cerium dioxide is formed, which is pure white. The oxide becomes yellow on heating, but the colour is lost on cooling if the heating has not been too intense or persistent. If the white oxide is strongly ignited in a blowpipe flame it shrinks visibly in volume and becomes slightly yellow. This change is probably due to polymerisation.

⁷³ A. Job, *Compt. rend.*, 1899, **128**, 178, 1098; *A.*, 1899, ii, 486.

⁷⁴ C. C. Meloche, *J. Amer. Chem. Soc.*, 1915, **37**, 2338; *A.*, ii, 776.

⁷⁵ E. Baur, *Zeitsch. anorg. Chem.*, 1902, **30**, 256; *A.*, 1902, ii, 398.

⁷⁶ J. F. Spencer, *T.*, 1915, **107**, 1265; *A.*, ii, 777.

Group V.

Some interesting investigations have been made on certain reactions with hydrazine.^{77, 78} Pure anhydrous hydrazine is prepared by boiling the partly dehydrated hydrazine hydrate for three hours under reflux with about a 50 per cent. excess of barium oxide. The hydrazine is then distilled under diminished pressure in an atmosphere of hydrogen. The product on analysis was found to contain 99.7 per cent. of hydrazine. Sodium derivatives of hydrazine may be prepared by the action of either metallic sodium or sodamide on anhydrous hydrazine. These substances are extraordinarily explosive, and from analysis appear to have the formulæ NaN_2H_3 and $\text{Na}_2\text{N}_2\text{H}_2$. The former compound has independently been prepared in glistening leaflets.⁷⁹

The solutions of the sodium hydrazides have been subjected to electrolysis, for they readily conduct electricity. Nitrogen and hydrogen are simultaneously evolved at both the anode and cathode. For each atom of copper deposited on the coulometer cathode, 1.1—1.5 atoms of nitrogen are liberated at the anode when the electrolyte is rather dilute. With a more highly concentrated solution the ratio $\text{Cu}:\text{N}$ varied from 1:2.1 to 1:2.6.

The solubilities have been determined of a considerable number of elements and inorganic salts in anhydrous hydrazine. Of the metallic elements the alkali metals are the only ones that are appreciably acted on and dissolved. The solubility increases with the atomic weight. Sulphur and iodine are very readily soluble, and chemical decomposition takes place with rapidity, especially in the latter case. The solubility of the metallic haloids appears to increase with the atomic weight of the halogen. In the case of the alkaline earth metals, crystals separate from the solutions on keeping, which are probably hydrazinated salts. The carbonates are at most only very sparingly soluble, whilst the oxides are insoluble. The nitrates, with the exception of those which react with the hydrazine, are, in the majority of cases, soluble. Sulphates and sulphides are only sparingly soluble. Ammonium salts, except triammonium phosphates, are soluble, with the evolution of much ammonia. This reaction is due to hydrazinolysis; bismuth chloride dissolves and reacts with the hydrazine, metallic bismuth being quantitatively precipitated. Cadmium carbonate and sulphide are insoluble, but the haloids are very readily soluble without any visible chemical reaction. The mercury salts, with the exception of

⁷⁷ T. W. B. Welsh, *J. Amer. Chem. Soc.*, 1915, **37**, 497; *A.*, ii, 256.

⁷⁸ T. W. B. Welsh and H. J. Broderson, *ibid.*, 1915, **37**, 816, 825; *A.*, ii, 337.

⁷⁹ W. Schlenk and T. Weichselfelder, *Ber.*, 1915, **48**, 669; *A.*, ii, 445.

mercuric sulphide, which is insoluble, react chemically with the hydrazine immediately with the formation of metallic mercury. It is very probable that nickel and cobalt salts dissolve and react chemically to form hydrazine additive compounds. In the case of cobalt chloride a slow, continuous decomposition takes place with the formation of a cobalt mirror. Copper and lead salts are all soluble with more or less decomposition, whilst in the case of silver salts the formation of a silver mirror is always observed.

A study of the reactions which occur with hydrazine as solvent has shown that the following take place. Cadmium and zinc sulphides can be precipitated by the action of hydrazine sulphide on those salts of these metals which are soluble in anhydrous hydrazine. A zinc hydrazide is probably precipitated when sodium hydrazide acts on a hydrazine solution of zinc chloride. Sodium precipitates the metals cadmium, zinc, and iron from solutions of their salts, but does not precipitate magnesium, calcium, and barium. In general, it may be said that reactions take place in anhydrous hydrazine similar to those which occur in water, liquid ammonia, and certain other dissociating solvents.

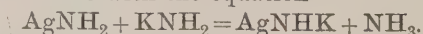
A further addition has been made to the work on the ammonia system of acids, bases, and salts. It has already been shown that the "ammono-acids" or acetamides react with potassamide in liquid ammonia. It is now found that salts may be obtained by using insoluble metallic amides, imides, or nitrides. A number of such compounds are described, such as silver benzenesulphonamide, $\text{SO}_2\text{Ph}\cdot\text{NHAg}\cdot 2\text{NH}_3$, cupric benzenesulphonamide,



and potassium acetobenzylamide, $\text{CH}_3\cdot\text{CO}\cdot\text{N}(\text{CH}_2\text{Ph})\text{K}\cdot\text{NH}_3$.⁸⁰

When potassamide is added in limited amount to a liquid ammonia solution of aluminium iodide a soluble ammonobasic iodide of aluminium is formed in accordance with the equation $2\text{AlI}_3 + 3\text{KNH}_2 = \text{Al}(\text{NH}_2)_3\cdot\text{AlI}_3 + 3\text{KI}$. At the ordinary temperature the salt separates with three molecules of ammonia of crystallisation, and at low temperatures a highly ammonated salt separates with 18 to 20 molecules of ammonia. If potassamide is added to the solution of this salt an insoluble ammonobasic aluminium iodide is precipitated, $\text{Al}(\text{NH}_2)_3\cdot\text{Al}(\text{NH}_2)_2\cdot\text{I}\cdot\text{NH}_3$, which on heating loses two molecules of ammonia to give $\text{Al}(\text{NH}_2)_3\cdot\text{AlNH}_2$.

Silver amide dissolves readily in a solution of potassamide in liquid ammonia. It is found that potassium ammonoargentate is formed. In accordance with the equation



⁸⁰ E. C. Franklin, *Proc. Nat. Acad. Sci.*, 1915, 1, 68; *J. Amer. Chem. Soc.*, 1915, 37, 847, 852; *A.*, i, 950; ii, 345, 348.

The compound separates from the concentrated solution in crystals with the composition $\text{AgNHK}, \text{NH}_3$.

This work has been extended to include the reactions between potassamide and salts of cadmium, nickel, and chromium.⁸¹ With cadmium thiocyanate or potassium cadmium cyanide, either cadmium amide, $\text{Cd}(\text{NH}_2)_2$, or potassium ammonocadmiate, $\text{Cd}(\text{NHK})_2, 2\text{NH}_3$, is formed according as to whether the cadmium salt or the ammono-base is in excess. The latter compound has already been described by Franklin. The former is a white powder which reacts violently with water, and when suddenly heated explodes, with liberation of metallic cadmium. When heated at 180° in a vacuum it loses ammonia, and is converted into cadmium nitride, Cd_3N_2 , a black, amorphous powder which explodes violently when brought into contact with water, and deposits metallic cadmium.

When approximately equivalent amounts of potassium nickel cyanide and potassamide are mixed, a lemon-yellow, curdy precipitate is formed. After a few washings with liquid ammonia this substance crumbles to a heavy powder having the composition $\text{K}(\text{CN})_2\text{Ni}\cdot\text{NHK}$. With a large excess of potassamide a deep red solution is formed, which on keeping yields deep red crystals having the composition $\text{Ni}_3\text{N}_{11}\text{H}_{22}\text{K}_7(\text{CN})_2$.

By varying the concentration of ammonia in ammonium hydroxide solutions of nickel thiocyanate, crystalline ammonia derivatives of this salt are formed with 2, 3, 4, and $5\frac{1}{2}$ molecules of ammonia. Under suitable conditions a fifth compound with $8\frac{1}{2}$ molecules of ammonia is produced. A solution of nickel thiocyanate in liquid ammonia when treated with an equivalent amount of potassamide solution gives a precipitate of nickel amide, $\text{Ni}(\text{NH}_2)_2$. This substance is a red, flocculent mass which when heated at 120° in a vacuum gives nickel nitride, Ni_3N_2 . The nickel amide dissolves in an excess of a potassamide solution to give a deep red solution, which deposits red crystals of aminopotassium nickel amide, $\text{Ni}_2\text{N}_3\text{K}_5, 6\text{NH}_3$.

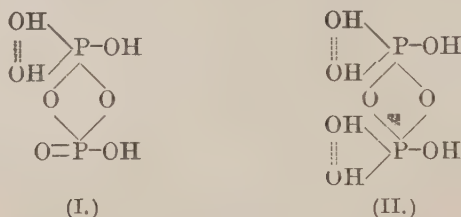
Pure red phosphorus has been obtained by the action of phosphorus tribromide on mercury.⁸² When a mixture of these two substances is heated in a sealed tube at $100\text{--}170^\circ$ for several days the product extracted with ether, and the residue again heated with phosphorus tribromide, there is obtained a pure red phosphorus as a cinnabar-red, micro-crystalline powder. The substance becomes brownish-black at 250° , but regains its colour on cooling and has D_4^{24} 1.876. It is insoluble in carbon disulphide, is not

⁸¹ G. S. Bohart, *J. Physical Chem.*, 1915, **19**, 537; *A.*, ii, 771.

⁸² L. Wolf, *Ber.*, 1915, **48**, 1272; *A.*, ii, 684.

blackened by ammonia, oxidises slowly in moist air, and inflames in air at approximately 300°.

Some work on the constitution of pyrophosphoric acid and some of its metallo-derivatives may be mentioned. In general, the properties of this acid suggests that it possesses an unsymmetrical structure.⁸³ The ionisation constants of the first two hydrogen ions are almost identical and very near that of the first ion of orthophosphoric acid. Those of the third and fourth hydrogen ions of pyrophosphoric acid are near to one another, but widely different from the first. It is suggested that the most probable formulæ for (I) pyrophosphoric acid and (II) orthophosphoric acid are:



The facts that pyrophosphoryl chloride, $P_2O_3Cl_4$, decomposes into $POCl_3$ and PO_2Cl when distilled under 10 mm. pressure, and that it reacts more violently with water than does phosphoryl chloride support the unsymmetrical constitution. Sodium pyrophosphate reacts with phosphorus pentachloride in a sealed tube above 200° according to the equation:



This reaction can only be accounted for by the unsymmetrical formula.

Many insoluble metallic pyrophosphates are soluble in alkali pyrophosphates to give solutions which fail to show many of the reactions of the metals. Several salts of complex metallo-pyrophosphoric acids have been prepared,⁸⁴ and it may be mentioned that they are analogous to the salts of ferriphosphoric acid.⁸⁵ By dropping a solution of manganese sesquioxide in cold concentrated hydrochloric acid into a saturated solution of sodium pyrophosphate, sodium manganipyrophosphate, $Na(MnP_2O_7) \cdot 5H_2O$, is obtained. Potassium forms two salts, $K(MnP_2O_7) \cdot 5H_2O$ and $3H_2O$, the former being pale violet and stable below 10°, whilst the latter is pale red and is decomposed only by boiling water. The salts

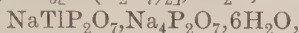
⁸³ D. Balareff, *Zeitsch. anorg. Chem.*, 1914, **88**, 133; *A.*, ii, 446.

⁸⁴ A. Rosenheim and T. Triantaphyllides, *Ber.*, 1915, **48**, 582; *A.*, ii, 463.

⁸⁵ R. F. Weinland and F. Ensgraber, *Zeitsch. anorg. Chem.*, 1913, **84**, 340; *A.*, 1914, ii, 132.

$\text{Ag}(\text{MnP}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ba}(\text{MnP}_2\text{O}_7)_2 \cdot 5\text{H}_2\text{O}$ are obtained by precipitation.

Similarly, the alkali metal chromiopyrophosphates, $\text{M}(\text{CrP}_2\text{O}_7)$, and sodium bismuthi- and molybdenopyrophosphates, $\text{Na}(\text{BiP}_2\text{O}_7) \cdot 3\text{H}_2\text{O}$, and $\text{Na}(\text{MoP}_2\text{O}_7) \cdot 12\text{H}_2\text{O}$, have been prepared. More complex derivatives are described, such as sodium thalloypyrophosphate, $\text{Na}_5[\text{Tl}(\text{P}_2\text{O}_7)_2] \cdot 6\text{H}_2\text{O}$, or



and two sodium ferripyrophosphates, $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Na}_8\text{Fe}_4(\text{P}_2\text{O}_7)_5 \cdot 28\text{H}_2\text{O}$.

Since cerium pyrophosphate is readily soluble in hydrochloric acid it may be noted that this may be used as a rapid and quantitative method of separating cerium and thorium, as was first discovered by Carney and Campbell.⁸⁶

Group VI.

The extensive use of elementary selenium as the basis of photoelectric cells and the value of these instruments in modern physical and astrophysical research is now fully recognised. A particularly sensitive form of selenium has been prepared.⁸⁷ If vitreous selenium, melted at 200° , is cooled rapidly under pressure it is transformed into a new variety, violet-grey in colour. It consists of slender crystals which are very sensitive photoelectrically, but very unstable. By using a solid solution of this substance in vitreous selenium it is possible to prepare a very sensitive photo-metric cell.

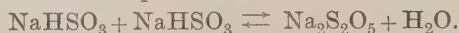
An interesting investigation has been made of the equilibrium conditions existing in aqueous solutions of sulphurous acid, the alkali metal hydrogen sulphites and metabisulphites.⁸⁸ The light absorptive power of sulphur dioxide as gas and in solution is well known, and it was thought possible that evidence might be gained of the constitution of the isomeric forms of metallic sulphites from a spectrophotometric examination of these salts. This expectation, however, has not been realised. When sufficient care has been taken in the preparation of the solutions it is found possible always to obtain the same values for the light absorptive power of sulphurous acid. It was otherwise, however, for the alkali metal hydrogen sulphite solutions, for the absorptive power was found in these to increase with time. Owing to the limits set by the apparatus, the most convenient strength was found to be $0.06\text{SO}_2/2$. Solutions of

⁸⁶ R. J. Carney and E. D. Campbell, *J. Amer. Chem. Soc.*, 1914, 36, 1134; *A.*, 1914, ii, 583.

⁸⁷ L. Angel, *Bull. Soc. chim.*, 1915, [iv], 17, 10; *A.*, ii, 163.

⁸⁸ C. S. Garrett, *T.*, 1915, 107, 1324; *A.*, ii, 714.

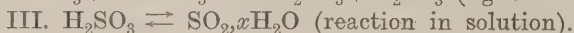
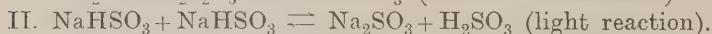
ammonium, sodium, potassium, and rubidium hydrogen sulphites were made, and their absorptive power examined from time to time. This was found to reach its maximum within about four to five weeks. A solution of sodium hydrogen sulphite was then freshly prepared, part being kept in the dark and part in the light. After twenty-six days both were examined, and while the light solution showed the maximum absorptive power, the dark solution exhibited only very little selective absorption. On exposing the dark solution to the light it developed in ten days a maximum absorption similar to the light portion, and remained constant. Similar results were obtained with solutions of the metabisulphites. Obviously, therefore, the seat of the light absorption does not lie in the equilibrium:



Again, the normal alkali sulphites exhibit no selective absorption even after long exposure to light. It may be mentioned that the region of selective absorption observed with the above solutions corresponds with that which appears in the spectrum of sulphur dioxide. The absorption cannot, however, be due to an hydrolysis of the ordinary type,



since in that case the absorptive power would decrease with the basicity of the metal, but the reverse is actually observed. The whole phenomena are to be explained by the reactions:



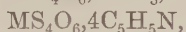
From the measurements of the absorptive power the relative quantities of $\text{SO}_2, x\text{H}_2\text{O}$ present in equivalent solutions of the various acid sulphites are calculated, and these quantities are found to increase with increasing strength of the base, that is to say, equilibrium II is shifted more to the right the stronger the parent base of the acid sulphite.

Mention may be made of work on the preparation and properties of the tetrathionates. The usual methods for the preparation of these compounds are unsatisfactory owing primarily to the fact that the presence of any thiosulphate accelerates the decomposition of the tetrathionate. Pure sodium and potassium tetrathionates can be prepared by the following method, in which the thiosulphate is not allowed to remain in presence of the tetrathionate.⁸⁹ To a cool solution of iodine in alcohol a saturated aqueous solution of sodium or potassium thiosulphate is added drop by drop. The

⁸⁹ A. Sander, *Zeitsch. angew. Chem.*, 1915, **28**, 273; *A.*, ii, 629.

tetrathionate, which separates as it is formed, is collected and washed with alcohol in order to free it from iodine and iodide. The salt is then dissolved in water and again precipitated by alcohol. After drying over sulphuric acid the salt may be kept for many months without undergoing decomposition. Aqueous solutions of tetrathionates slowly decompose, the principal reaction being $\text{K}_2\text{S}_4\text{O}_6 = \text{K}_2\text{SO}_4 + \text{SO}_2 + 2\text{S}$. Some thiosulphate is, however, formed at the same time. The decomposition is very slow even at 100° , but the presence of thiosulphates catalyses the reaction.

Tetrathionic and persulphuric acids not only possess similar constitutions, $\text{OH}\cdot\text{SO}_2\cdot\text{S}\cdot\text{S}\cdot\text{SO}_2\cdot\text{OH}$ and $\text{OH}\cdot\text{SO}_2\cdot\text{O}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ respectively, but exhibit various analogies.⁹⁰ The tetrathionates form with ammonia, pyridine, and hexamethylenetetramine compounds corresponding in composition, external form, and solubility with those given by the persulphates.⁹¹ Compounds of hexamethylenetetramine with magnesium, cobalt, and nickel tetrathionates, like those of the corresponding persulphates, contain $8\text{H}_2\text{O}$. The following have been prepared: $\text{ZnS}_4\text{O}_6\cdot 4\text{NH}_3$, $\text{NiS}_4\text{O}_6\cdot 6\text{NH}_3$,



where M stands for zinc, cadmium, copper, nickel, and cobalt; $\text{MS}_4\text{O}_6\cdot 2\text{C}_6\text{H}_{12}\text{N}_4\cdot 8\text{H}_2\text{O}$, where M stands for magnesium, nickel, and cobalt.

Group VII.

Some new measurements of the vapour pressure of iodine have been made between 50° and 95° ⁹² which form an extension of some earlier measurements between 0° and 55° .⁹³ The method employed was the passage of a measured volume of air over pure iodine. The air and iodine were passed into a solution of sodium carbonate, which was afterwards acidified. The liberated iodine was reduced with hydrazine and then precipitated as silver iodide. The results, together with those of the previous investigation, can be expressed by $\log p = -106\cdot3930 + 46\cdot611 \log T - 0\cdot031677T$, and still better by $\log p = 9\cdot7522 - 2863\cdot54/(T-19)$.

If iodine is dissolved in anhydrous perchloric acid, cooled by ice and salt, and the solution oxidised with ozone, iodine perchlorate, $\text{I}(\text{ClO}_4)_3\cdot 2\text{H}_2\text{O}$, separates in greenish-yellow needles which may be

⁹⁰ F. Calzolari, *Atti R. Accad. Lincei*, 1915, [v], **24**, i, 921; *A.*, ii, 629.

⁹¹ G. A. Barbieri and F. Calzolari, *Zeitsch. anorg. Chem.*, 1911, **71**, 347; *A.*, 1911, ii, 889.

⁹² G. P. Baxter and M. R. Grose, *J. Amer. Chem. Soc.*, 1915, **37**, 1061; *A.*, ii, 416.

⁹³ G. P. Baxter, C. P. Hickey, and W. C. Holmes, *ibid.*, 1907, **29**, 127; *A.*, 1907, ii, 253.

washed with cold perchloric acid. The reaction takes place as follows: $I_2 + 6HClO_4 + O_3 = 2I(ClO_4)_3 + 3H_2O$.⁹⁴

On heating basic iodine sulphate with sulphur trioxide in a sealed tube at 100—120° for one hundred and forty hours, iodine sulphate, $I_2(SO_4)_3$, is obtained in yellow crystals. Iodine iodate, $I(IO_3)_3$, is formed on warming iodic acid with concentrated phosphoric acid (D 1.70).

The statements made as to the preparation of the various modifications of manganese sulphide are somewhat contradictory, and methods are given for the preparation of these without difficulty.⁹⁵ The green modification may be prepared by the addition of freshly-prepared ammonium hydrogen sulphide to a solution of manganous chloride or sulphate containing some ammonium chloride. The rose-coloured modification is first precipitated, but soon changes into the green modification. If hydrogen sulphide is passed for some time through a faintly acid solution of a manganous salt the red modification is precipitated. Rose-coloured manganese sulphide is precipitated by the addition of an alkali sulphide to a solution of a manganous salt. Both the rose and red varieties are converted into the green modification by trituration.

E. C. C. BALY.

⁹⁴ F. Fichter and H. Kappeler, *Zeitsch. anorg. Chem.*, 1915, **91**, 134; *A.*, **ii**, 253.

⁹⁵ V. M. Fischer, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1481, 1519; *A.*, **ii**, 462, 487.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

It may at once be said that the review of the literature of the past year dealing with the chemistry of aliphatic compounds has not proved to be a particularly satisfactory task. Although there is, on every hand, abundant evidence that research of the most varied and valuable nature is at present being vigorously prosecuted, it is, nevertheless, not from the pages of the scientific journals that this information is to be gleaned. Recent publications, in fact, give little or no index of the directions in which most of the research on organic compounds is now being conducted, and although much might be said as the result of an examination of recent patent specifications, it would not be in harmony with the character of the Annual Reports to limit the account of the year's work to technical applications of the science. This state of affairs is, after all, only a natural consequence of the abnormal conditions which prevail, but the impression left in the mind of the reviewer after an impartial scrutiny of the literature, both home and foreign, is that the purely scientific advances recorded during the year in this branch of the subject have indeed been meagre.

The bulk of the journals remains very much the same as usual. The number of papers, and the general nature of the problems described, also show an apparent similarity to those of previous years, but the papers themselves generally lack a definite objective, and are in many cases interim communications published with the view of disposing of incompleated topics. This tendency, which is recognisable in journals from all sources, may be unavoidable, but is an aggravation of what was in normal times a regrettable feature in many publications.

With these factors in operation, the present Report must of necessity differ in many respects from its predecessors. Several important branches of aliphatic chemistry automatically disappear from the review owing to a reason which must appeal to all workers in this branch of the subject—lack of the necessary material.

With these restrictions, it has been no easy matter to weave the isolated results into a connected narrative, and no apology is needed for the fact that different groups of compounds are treated in widely varying detail, which, on first inspection, might appear disproportionate.

Hydrocarbons.

Substances which are in universal and urgent demand are unlikely to be the subject of detailed scientific examination so long as attention is, for the time being, focussed on their economical production and use. It is therefore not surprising to find that, during the period under review, the simpler hydrocarbons have been studied by the engineer rather than by the chemist, and that the pages of the scientific journals contain few references to these compounds. After a search through patent and statistical literature it is almost refreshing to fall back upon the strictly academic discussion as to the origin of petroleum, which is still being continued with some vigour. The great efficiency of catalysts, and the controlling influence of pressure in promoting the synthesis of hydrocarbons of varied constitution, have again been quoted in support of the idea that natural paraffins arise from inorganic sources, and not from biological decompositions.¹ It is perhaps well that such views should be freely ventilated, as they may lead to results of practical importance, but if they are accepted it is difficult to explain away the existence of optically active petroleum, even by the ingenious suggestion² that, as the primary cause of optical activity in organisms is unknown, the occurrence of the phenomenon in natural paraffins is no index of their origin. Evidently much systematic work remains to be done on this subject before any definite conclusions can be drawn, but it would appear that if the statement that the optical activity of mineral oils is diminished by exposure to a high temperature can be definitely verified, or refuted, the whole question would be finally settled.³

So far as aliphatic hydrocarbons are concerned, the chief interest of the synthetic chemist is evidently, for the present, centred on the reactions of unsaturated members. Catalytic methods of hydrogenation continue to attract much attention, but show little variety, either in the choice of catalysts or in the conditions under which they are used, although there is a natural tendency to avoid processes which involve either high temperature or heavy pressures. There is also little progress to report in connexion with

¹ N. Kishner, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1428; *A.*, ii, 473.

² A. E. Tschitschibabin, *ibid.*, 1915, **47**, 714; *A.*, i, 637.

³ C. Engler and W. Steinkopf, *Ber.*, 1914, **47**, 3358; *A.*, i, 205.

the caoutchouc problem, although Harries has contributed a lengthy paper,⁴ where many new experimental facts are recorded, which lead to still another formula for natural caoutchouc. It is difficult to resist the feeling that, in this respect, we are called on to change our ideas too frequently, and it may be well to delay any detailed discussion of these results, but the essential idea in the new formula is the construction of a C_{20} ring by the repetition of the group $\cdot CH_2 \cdot CH : CMe \cdot CH_2 \cdot$ five times. The structure thus obtained certainly accounts readily for the facts that at least two distinct varieties of "regenerated caoutchouc" are known, and that the ozonides obtained from them yield different decomposition products, but the time has not yet come for the final adoption of a structural formula for the caoutchouc complex, particularly as the controversy regarding the polymerisation products obtained from pure isoprene is still unsettled.⁵ Apparently, however, there is no inherent objection to the adoption of a homocyclic structure containing no fewer than twenty carbon atoms, as evidence is accumulating which points to the idea that the stability of a ring system is affected by many other considerations than that of tension alone.⁶

Greater satisfaction is found in directing attention to the varied and useful reactions which are now being carried out with acetylene. Although foreshadowed by the work of the past three or four years, this development has now assumed amazing proportions, and has opened up the way for many processes of technical importance. It is almost impossible to give an idea of the variety of the synthetical reactions based on acetylene, particularly when promoted by catalysts, but an excellent account, which deals with fundamental examples, has been contributed by Tschitschibabin.⁷

The conditions are there described under which acetylene reacts with ammonia to give several pyridine bases, the reaction probably taking place through the intermediate formation of aldehyde-ammonia. Similarly, the hydrocarbon reacts with hydrogen sulphide to give thiophen, apparently in good yield and in a condition readily purified. Of considerable interest, also, is the statement that acetylene, in contact with alumina, is converted at 400° into a mixture of aromatic hydrocarbons in which benzene is present to the extent of less than 10 per cent. From the results of other investigations it is probable that the methyl homologues of benzene are formed in this reaction, and there is much to be

⁴ C. Harries, *Annalen*, 1914, **406**, 173; *A.*, i, 277.

⁵ C. Harries, *Ber.*, 1915, **48**, 863; *A.*, i, 703.

⁶ N. A. Rosanov, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 591; *A.*, i, 657.

⁷ A. E. Tschitschibabin, *ibid.*, 703; *A.*, i, 638.

said for the suggestion,⁸ recently revived, that the reactions of acetylene are responsible for the formation of the coal-tar hydrocarbons and their accompanying derivatives. This idea is further supported by the observation that phenol is produced in reactions in which certain transformations of acetylene were carried out under free access of air. The field of technical application which is opened out by these results promises to be highly fruitful, particularly as various other reactions of acetylene have now been utilised in patented processes. Thus, the conversion of the hydrocarbon into acetaldehyde by the action of acids containing mercury salts⁹ has by simple modifications¹⁰ been elaborated into methods for obtaining acetic acid.

From every point of view it may be said that the study of unsaturated aliphatic hydrocarbons is in a satisfactory condition, as new problems are continually being unfolded, which are not only in themselves of great interest, but give promise of highly important applications.

Alcohols and their Derivatives.

Although the simpler aliphatic alcohols are at present the subject of much investigation, the results are seldom to be found in the literature, and, in addition, the references to such closely related derivatives as aldehydes and ketones are, for the most part, meagre and unattractive. No useful purpose would be served by summarising any but a few of the papers which deal with this branch of the subject, but reference may be made, in passing, to a few specific reactions that have led to the formation of important individual substances or mark an advance in experimental methods.

Thus, for example, Wohl describes an extension of his work on the synthesis of aldehydes through the agency of the corresponding acetals,¹¹ which has resulted in the isolation of glyceraldehyde in *d*- and *l*-forms. The resolution into active constituents was effected by treating *r*- β -aminolactaldehyde dimethylacetal with *l*-menthylcarbimide and separation of the active carbamides thus formed by crystallisation. The process was obviously not unattended with difficulties, and, after removal of the amino-group by means of nitrous acid followed by hydrolysis under mild conditions with dilute sulphuric acid, the corresponding active forms of glyceraldehyde were obtained, unfortunately only as syrups. A

⁸ R. Meyer and H. Fricke, *Ber.*, 1914, **47**, 2765; *A.*, i, 207.

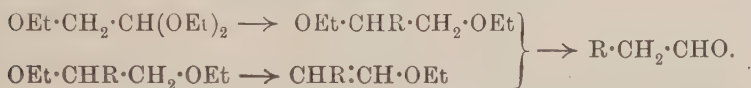
⁹ *Fr. Pat.*, 474246; *A.*, i, 773.

¹⁰ *Fr. Pat.*, 473158; *A.*, i, 645; *Fr. Pat.*, 467778; *A.*, i, 2; *Fr. Pat.*, 467515; *A.*, i, 2.

¹¹ A. Wohl und F. Momber, *Ber.*, 1914, **47**, 3346; *A.*, i, 216.

significant statement made in the original paper is that these products polymerise with ease, and this suggests that the direct synthesis of the active fructoses and sorboses may yet be carried out on the lines laid down by Schmitz.¹²

Research of the above nature on unstable aldehydes has undoubtedly made great progress in recent years, and mention should be made of a reaction which may add to the number of these compounds available for examination. By means of a standard application of the Grignard reagent one of the two alkyloxy-groups of an acetal may be eliminated, saturation being, of course, completed by the addition of an alkyl group. Taking ethoxyacetal as an example,¹³ two products result, which yield, on hydrolysis, the same substituted acetaldehyde:



The mechanism of the final hydrolysis evidently differs in the two cases mentioned above, but the process appears capable of considerable application, and may prove useful, although the hope always remains that, with the extensive study of catalysts now in progress, the universal method of preparing aldehydes may yet be found in the oxidation of the corresponding alcohol. It would be very desirable if the formation of ketones could be similarly controlled.

Polyhydroxy-compounds.—Work on these compounds has for the most part followed standard lines, but nevertheless presents some features of interest. Thus, for example, it has been shown that the tendency displayed by ethylene glycol to be transformed into acetaldehyde extends to other compounds of the general type $\text{CH}_2\text{X} \cdot \text{CH}_2\text{Y}$, and the change may be brought about by very simple reagents.¹⁴ This is an important observation, as the capacity of the group $\text{CH}_2(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot$ to pass into $\text{CH}_3 \cdot \text{CH} <$ in simple reactions has a direct bearing on the vexed question of the mechanism of fermentation. It may be noted at this stage that the use of Grignard reagents in the preparation of glycols frequently gives rise to irregular results, and fresh examples illustrating this lack of uniformity have recently been encountered.¹⁵ For example, starting with ethyl dimethylmalonate and magnesium methyl iodide, the essential products obtained were



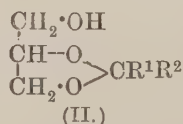
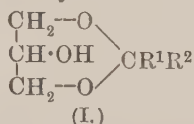
¹² *Ann. Report*, 1913, 77. ¹³ E. Späth, *Monatsh.*, 1915, 36, 1; *A.*, i, 262.

¹⁴ C. Neuberg and B. Rewald, *Biochem. Zeitsch.*, 1914, 67, 127; *A.*, i, 214. C. Neuberg and O. Rubin, *ibid.*, 77; *A.*, i, 215; C. Neuberg, *ibid.*, 71; *A.*, i, 214.

¹⁵ A. Kalischev, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 427; *A.*, 1914, i, 918.

This tendency of the ester groups to react unequally is more pronounced when ethyl diethylmalonate is similarly treated, as in this case no glycol was formed. The same result was also obtained when homologues of methyl iodide were employed in the preparation of the Grignard reagent, and the generalisation is made that the normal reaction only proceeds smoothly according to the molecular proportions $\text{CR}^1\text{R}^2(\text{CO}_2\text{Et})_2 + 4\text{MgR}^3\text{I}$, where R^1 , R^2 , and R^3 represent methyl groups.

The subject of ring formation from glycols has also received attention,¹⁶ and it is evident, in the glycol series at all events, that the general principles governing the formation of alkylene oxides are not yet fully understood. On the other hand, definite evidence is now available which establishes the constitution of the cyclic structures formed when polyhydroxy-compounds enter into condensation with aldehydes or ketones, a problem bearing on synthetical work in the sugar group. Taking glycerol as an example, the two alternative formulæ of these derivatives may be represented by



and in the case of glycerol *isopropylidene ether* and glycerol *benzylidene ether* both compounds are constituted according to formula II.¹⁷ The method adopted was to methylate the compounds and, by hydrolysis, to isolate the corresponding glycerol methyl ether. In each case the same product resulted, and the methyl group was shown to be situated in the α -position. The structure thus established seems to be general in its application and extends to methyleneglycerol, which is resolvable into active components, and thus also corresponds with formula II.¹⁸ Work of this nature is obviously capable of extension to the problem of solving the constitution of the glycerophosphoric acids, although it is to be noticed that a distinct advance has been made in this subject during the year. Thus, α -glycerophosphoric acid has been synthesised¹⁹ by the oxidation of sodium allyl phosphate, and an experimental method devised whereby the α - or β -substitution of the glycerophosphates may be determined with some degree of certainty.²⁰ As the whole question of the preparation of esters

¹⁶ A. Franke and F. Lieben, *Monatsh.*, 1914, **35**, 1431; *A.*, i, 490.

¹⁷ J. C. Irvine, J. L. A. Macdonald, and C. W. Soutar, *T.*, 1915, **107**, 337; *A.*, i, 209.

¹⁸ D. H. Peacock, *ibid.*, 815; *A.*, i, 767.

¹⁹ O. Bailly, *Compt. rend.*, 1915, **160**, 663; *A.*, i, 492.

²⁰ L. Grimbert and O. Bailly, *ibid.*, 207; *A.*, i, 73.

from glycerol is beset with difficulties, attention may with advantage be drawn to a number of papers which are suggestive in their experimental details. Thus, the varying effect of different catalysts in the preparation of triacetin has been ascertained,²¹ and although it is shown that sulphuric acid is the most effective catalyst, the fact that less energetic reagents may be employed with advantage will find applications. Another useful practical detail is mentioned in a description²² of the preparation of $\beta\gamma$ -distearin. As is well known, the production of this and similar compounds from $\beta\gamma$ -dibromopropyl alcohol is complicated by the simultaneous formation of triglycerides and fatty acids. These difficulties may be overcome by the substitution of lead salts for sodium salts, and although the yield of distearin in the particular reaction now under consideration did not exceed 20 per cent., the result must be considered satisfactory.

Turning to related problems, the study of mixed glycerides, which recently promised to add materially to the interest of this section of the subject, has languished during the past two years, although there seems no good reason why the complete structure of these important compounds should not be fully determined with the experimental methods now available. Then, again, the catalytic reduction of unsaturated fats having been brought within the range of manufacturing processes is another subject which is now less prominent in the literature than formerly. This is, of course, a perfectly natural development, and recent papers have, for the most part, been restricted to the academic discussion as to whether metallic nickel or an oxide of nickel is the responsible agent in catalytic hydrogenation. The evidence is now clearer than two years ago, and reference may be made to two investigations²³ the results of which, taken conjointly, point emphatically to the idea that metallic nickel is an inferior reagent in this important reaction to the oxide or other oxy-compounds.

In last year's Report attention was drawn to the fact that the configuration of optically active polyhydric alcohols involves considerations which are usually ignored. In a compound of this nature, such as the alcohols related to the sugars, the terminal $\text{CH}_2\cdot\text{OH}$ groups apparently do not possess the property of free rotation, but in virtue of the attractive and repulsive forces exercised by the remaining hydroxyl groups assume preferentially

²¹ J. B. Senderens and J. Aboulenc, *Compt. rend.*, 1914, **158**, 581; *A.*, 1914, i, 379.

²² R. R. Renshaw, *J. Amer. Chem. Soc.*, 1914, **36**, 537; *A.*, 1914, i, 477.

²³ E. Erdmann, *J. pr. Chem.*, 1915, [ii], **91**, 469; *A.*, i, 770; W. Siegmund and W. Suida, *ibid.*, 442; *A.*, ii, 626.

fixed positions. The idea was originally put forward to explain certain reactions of mannitol, and has now been tested by physical methods.²⁴ Mannitol, $\epsilon\zeta$ -dimethyl mannitol, and $\gamma\delta\epsilon\zeta$ -tetramethyl mannitol all possess the property of increasing the conductivity of boric acid to very much the same extent, while other methylated mannitols give negative results. Again, mannitolmonoacetone and mannitoldiacetone occasion only very slight changes in the conductivity of boric acid, so that evidently the two terminal hydroxyl groups of the parent mannitol are differently arranged in space relatively to the neighbouring hydroxyl groups. The results thus substantiate the formula for mannitol which was referred to last year, and point to the existence of a new complexity in a subject already sufficiently complex.

Before leaving this subject, mention should be made of another method whereby the properties of fractions of polyhydroxy-molecules may be studied. Partly methylated derivatives of these compounds are already known, and similar compounds in which some of the hydroxyl groups are replaced by acyl residues have recently been described.²⁵ Compounds of this type offer many opportunities for structural research, and a single example will indicate sufficiently clearly how they are obtained. Mannitoltri-acetone was converted by partial hydrolysis into mannitolmonoacetone, which, by the action of benzoyl chloride in presence of a base, was acylated to give tetrabenzoylmannitolmonoacetone. When hydrolysed under mild conditions the unstable acetone residue was removed, and a tetrabenzoylmannitol was thus formed. The examples quoted in the original paper are sufficiently striking to show that the principles involved are of general application, and, as already stated, the future possibilities of these compounds are of the utmost importance.

The Sugar Group.

In last year's Report it was indicated that current views regarding the structure of the reducing sugars are in a state of fluctuation, and that future research would add further complications to the constitution of even the simpler carbohydrates. In this connexion attention was drawn to Fischer's discovery of a third form of methylglucoside,²⁶ the existence of which might be dependent on a new, and hitherto unsuspected, type of attachment of a methyl group to the reducing group of the sugar, or, alternately, to a

²⁴ J. C. Irvine and Miss E. S. Steele, *T.*, 1915, **107**, 1221; *A.*, ii, 669.

²⁵ E. Fischer, *Ber.*, 1915, **48**, 266; *A.*, i, 118.

²⁶ *Ber.*, 1914, **47**, 1980; *A.*, i, 57.

different internal linking in the sugar molecule. The second of these alternatives is the more attractive, as its adoption involves the recognition of new types of reducing sugars. There is now no doubt, in the particular case of glucose at least, that the oxygen atom of the ring may connect not only the α - and δ -carbon atoms, but other pairs of atoms as well. Thus, it has been shown²⁷ that Fischer's " γ -methylglucoside" is a mixture of two stereoisomerides, and, on methylation followed by hydrolysis, gives rise to a form of tetramethyl glucose different from that prepared from α - or β -methylglucoside. This at once proves the existence of a new form of glucose, resembling the γ -oxidic varieties with respect to glucoside formation, but differing in a remarkable degree in its behaviour towards most reagents. As this form of the sugar, termed provisionally " γ -glucose," has not been isolated in the free state, its properties can only be deduced from those of the corresponding tetramethylated derivative, but it is evident that its reactivity far exceeds that of α - or β -glucose. Thus, the compound enters into condensation with alcohol with extreme ease, and reduces alkaline permanganate solution instantly. In the latter case, the reaction gives rise to a new form of tetramethylgluconic acid, which, in turn, may be converted into an isomeric variety of tetramethylgluconolactone. From this result, and from the evidence afforded by reduction, the formulæ provisionally ascribed to tetramethyl γ -glucose and to the parent sugar from which it is derived are



In all probability the other reducing sugars exist in similar forms, and thus a most extensive field of research awaits development. It is highly desirable that the structure of γ -glucose should be definitely settled, as it is most unlikely that derivatives of this specially reactive form of a common sugar are unrepresented in important natural processes, but many experimental difficulties stand in the way. In the future development of the problem the characterisation of β - and γ -lactones of the hexonic acids will doubtless play an important part, and the work on this subject inaugurated by Nef is invested with a new interest, and is fortunately being continued.²⁸

Another experimental development in the sugar group, the results of which should in time be far-reaching, is the preparation of definite derivatives in which selected hydroxyl groups are substi-

²⁷ J. C. Irvine, A. W. Fyfe, and T. P. Hogg, *T.*, 1915, **107**, 524; *A.*, i, 381.

²⁸ O. F. Hedenburg, *J. Amer. Chem. Soc.*, 1915, **37**, 345; *A.*, i, 76.

tuted while the remaining hydroxyl groups are exposed, and can thus take part in further reactions. The partially methylated sugars were the first representatives of this type of compound, and their preparation has opened up the way for the production, on similar lines, of other derivatives. Up to the present, however, the experimental work in this field has to a large extent been applied to polyhydric alcohols rather than to sugars, and this is an advisable preliminary in dealing with the members of the sugar group, but a considerable advance has been made by clearing up the many difficulties which attend the preparation of glucose-monoacetone.²⁹ Reference has already been made to the preparation of dibenzoyldulcitol and tetrabenzoylmannitol³⁰ by acylation of the corresponding isopropylidene compounds, followed by the removal of acetone by gentle hydrolysis. It is easy to see that these compounds will receive useful application in sugar synthesis, but in the meantime attention may be drawn to a simpler but less effective method of combining different acyl groups with the sugar molecule.³¹

By decomposing tetra-acetylbromoglucose with silver benzoate, a benzoyltetra-acetyl- β -glucose has been obtained, and the general reaction is capable of wide variation, although it is difficult to see what the ultimate object of synthetical work of this description may be beyond improving the details of general practical methods.

Interest is, however, attached to a series of papers by Hudson and his pupils describing the properties and constants of a number of penta-acetates of simple sugars as prepared by well-developed processes. Many interesting points are raised in these papers, particularly the observation that galactose penta-acetate exists in three distinct forms.³² The variety of the compound first isolated by Erwig and Koenigs, and subsequently described by Fischer and Armstrong, melts at 142° and shows $[\alpha]_D + 25^{\circ}$ in chloroform solution. As is usually the case with such compounds, when boiled with acetic anhydride and zinc chloride it is converted into an isomeric variety (m. p. 95.5°) which is strongly dextrorotatory in all solvents. It is now shown that the direct acetylation of the sugar gives rise to a third, more soluble, penta-acetate, the melting point of which is not far removed from 95° , but which is decidedly laevorotatory. There is a strong probability that this compound is derived from a form of galactose corresponding with the new γ -glucose, particularly as evidence already exists pointing

²⁹ J. C. Irvine and J. L. A. Macdonald, *T.*, 1915, **107**, 1701.

³⁰ E. Fischer, *loc. cit.*

³¹ G. Zemplén and E. D. László, *Ber.*, 1915, **48**, 915; *A.*, i, 651.

³² C. S. Hudson and H. O. Parker, *J. Amer. Chem. Soc.*, 1915, **37**, 1589; *A.*, i, 652; C. S. Hudson, *ibid.*, 1591; *A.*, i, 651.

to the fact that galactose shows a distinct tendency to form derivatives of three types.³³ The examination of the rotatory powers of isomeric α - and β -penta-acetates of sugars has also been continued with the object of testing Hudson's generalisations on this subject, with the general result that fresh evidence in support of this theory has been obtained. Thus, the sum of the molecular rotations of the glucose penta-acetates is in good agreement with the same value determined for the two acetylated methyl glucosides when the rotations are taken in solvents other than benzene.³⁴ This disposes of an apparent exception to Hudson's rule.

Other problems connected with the optical activity of sugars continue to attract workers, and, in particular, the phenomenon of mutarotation has received considerable attention. The vexed question of the part played by water in promoting the change $\alpha \rightleftharpoons \beta$ in a reducing sugar has again been raised, and results obtained which, on first inspection, appear to be contradictory. It has been shown, for example, that the mutarotation of sugars proceeds normally in anhydrous formamide solution,³⁵ the solutes also showing a normal molecular weight in this solvent. This evidence is certainly opposed to the hydrate theory of mutarotation, but, on the other hand, a definite proof is now available that in aqueous solution the rotatory changes are due to association with the solvent. When tetramethyl α -glucose, which contains only one hydroxyl group, is dissolved in dilute aqueous boric acid solution the conductivity of the system gradually rises to a maximum, which persists when mutarotation is complete. The reasonable deduction from this result is that a second hydroxyl group becomes attached to the sugar molecule, and that the final equilibrium is not between the simple α - and β -sugars, but between the corresponding oxonium hydrates.³⁶ The deductions made in the paper now under discussion are, of course, dependent on the principle established by Böeseken³⁷ that exaltation in the conductivity of boric acid is only induced by compounds where two hydroxyl groups are attached to neighbouring carbon atoms. It may be noted, however, that numerous results recently to hand substantiate Böeseken's views,³⁸ and indicate that they may be applied to consti-

³³ J. C. Irvine and A. Cameron, *T.*, 1905, **87**, 900.

³⁴ C. S. Hudson and J. K. Dale, *J. Amer. Chem. Soc.*, 1915, **37**, 1264; *A.*, i, 501.

³⁵ J. E. Mackenzie and S. Ghosh, *Proc. Roy. Soc. Edin.*, 1914-15, **35**, 22; *A.*, ii, 301.

³⁶ J. C. Irvine and Miss E. S. Steele, *T.*, 1915, **107**, 1230; *A.*, ii, 661.

³⁷ *Ann. Report*, 1913, 79.

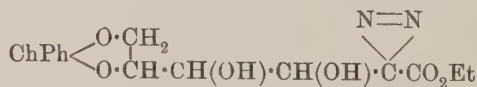
³⁸ J. Böeseken and pupils, *Rec. trav. chim.*, 1915, **34**, 96; *A.*, ii 136; *ibid.*, 272; *A.*, ii, 667.

tutional problems with a considerable amount of certainty, particularly as they are supported by the results of other physical investigations.³⁹ Returning to the problem of mutarotation, it would appear that the mechanism of the process varies with the nature of the solvent employed, but the whole question, like every other problem in the sugar group, is rendered vague and uncertain until it has been shown what part (if any) is played in the process by isomeric forms of the sugar conforming to the γ -type.

Although numerous processes are available whereby reducing sugars may be degraded to lower members, they generally offer considerable experimental difficulty, and a simple method of effecting such changes will be welcomed, particularly as it seems to be of general application and to give good yields. When gluconolactone in alcoholic solution is saturated with ammonia, *d*-gluconamide is formed, and this, on subsequent treatment with hypochlorous acid, is decomposed according to the scheme:



The change is thus an application of the Hofmann reaction, and the fact that a 50 per cent. yield of *d*-arabinose was obtained in the example quoted above speaks for itself sufficiently.⁴⁰ Before leaving the subject of the simpler carbohydrates, attention should be drawn to two important papers which deal with structural problems of some interest. In the course of a research,⁴¹ the initial object of which was apparently the elimination of the amino-group from the glucosamic acid residue, nitrous acid was allowed to act on ethyl benzyldieneglucosamate. Under these conditions of substitution, it might have been expected that the customary dehydration which accompanies this reaction in the case of glucosamine derivatives would have been avoided, but the unexpected result was the formation of a diazo-ester:



This reaction may be manipulated to explain the Walden inversion already recorded in the conversion of glucosamine into either glucose or mannose, but it is in some ways opposed to the view⁴² that the essential action of nitrous acid on amines is the formation of the simple nitrite. The result mentioned above is, however, of

³⁹ G. Calcagni, *Gazzetta*, 1914, **44**, ii, 447; *A.*, ii, 14.

⁴⁰ R. A. Weerman, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1163; *A.*, i, 387.

⁴¹ P. A. Levene and F. B. La Forge, *J. Biol. Chem.*, 1915, **21**, 345; *A.*, i, 786.

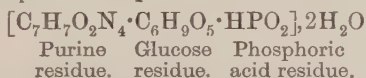
⁴² P. Neogi, *T.*, 1914, **105**, 1270.

considerable importance, particularly as evidence is now available⁴³ that chitose may be regarded as $\alpha\delta$ -anhydromannose.

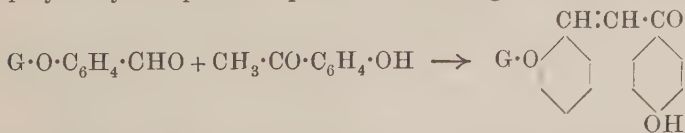
Glucosides.

After a period of marked activity and success, the biochemical synthesis of glucosides by means of enzymes has in the past year failed to yield any outstanding results. Although numerous papers on this subject have appeared,⁴⁴ they are, for the most part, records of tedious processes and experimental difficulty. This is not surprising considering the nature of the hydroxy-compounds coupled with the sugar residue.

On the other hand, by means of methods more familiar to the organic chemist, several important glucoside syntheses have been effected. In particular, attention should be drawn to the use made by Fischer of theophyllineglucoside, one of the purine glucosides already described by him. The introduction of a phosphoric acid residue into the compound, and the consequent synthesis of a definite nucleotide, is not only in itself of great importance, but the experimental method adopted is probably quite general in its application. The essential reagent employed was phosphoryl chloride, and the reaction, which was carried out in pyridine solution, ultimately yielded hydrated theophyllineglucosidephosphoric acid, to which the empirical formula:



is ascribed.⁴⁵ This successful development of glucoside synthesis is most gratifying, but is evidently surrounded by profound experimental and constitutional difficulties. Other examples of increasing the substitution in glucosides are furnished by the alkaline condensation of helicin with various hydroxy-ketones.⁴⁶ Taking one specific case in illustration, the reaction between the glucoside and *p*-hydroxyacetophenone proceeds according to the scheme:



where G represents the sugar residue. The essential reaction involved is, of course, a standard one, but the research is worthy

⁴³ P. A. Levene and F. B. La Forge, *J. Biol. Chem.*, 1915, **21**, 351; *A.*, i, 782.

⁴⁴ E. Bourquelot, M. Bridel, and A. Aubry, *Compt. rend.*, 1915, **160**, 214, 571, 674, 823; **161**, 41; *A.*, i, 76, 382, 501, 703, 829.

⁴⁵ E. Fischer, *Ber.*, 1914, **47**, 3193; *A.*, i, 296.

⁴⁶ G. Bargellini, *Gazzetta*, 1914, **44**, ii, 520; *A.*, i, 62.

of mention, as the synthesis of glucosides with long side-chains is of great importance, and must be extended so as to throw light on the general mechanism of cleavage reactions.

In other respects, the synthesis and examination of glucosides have proceeded on perfectly normal lines.

Disaccharides and Polysaccharides.

Comparatively few papers dealing with this division of the carbohydrates have appeared during the past year, and the results described are frequently amplifications or corrections of old observations. Some points, however, should be noted. Those who have worked with maltose or lactose are well aware of the difficulty in fixing standard values for the melting points or specific rotations of simple derivatives of these sugars, the identification of which is in consequence restricted to osazone-formation. In the case of the octa-acetates, the values have now been standardised.⁴⁷ The important point emerges in the course of this work that benzene is not a suitable solvent in which to compare specific rotations in the sugar group, and, further, evidence is furnished that the linking of the glucose and galactose residues in lactose is the same as that of the two glucose residues in cellulose. This is an important observation which, in time, may be of value when the structure of cellulose once more receives attention.

Naturally enough, investigations on cellulose have recently found no place in the scientific literature, but some progress has been made in the study of the structure of starch. It has been shown⁴⁸ that, by biochemical agency, rice starch may be degraded into definite polyamyloses in much the same manner as potato starch. Whatever prospect there may be, however, of solving the question of the constitution of the starch complex by this or other methods is seriously affected by the increasing evidence that the small phosphorus-content in starch is not adventitious, but exists as a definite combined constituent.⁴⁹

It is with considerable diffidence that any reference is made to recent papers by Panzer,⁵⁰ in which it is claimed that, when certain carbohydrates are acted on successively with hydrogen chloride and ammonia, the products acquire diastatic properties. This result, if substantiated, is of obvious importance, and is evidently the outcome of Panzer's earlier work on the action of these reagents

⁴⁷ C. S. Hudson and J. M. Johnson, *J. Amer. Chem. Soc.*, 1915, **37**, 1270; 1276; *A.*, i, 502, 503.

⁴⁸ H. Pringsheim and F. Eissler, *Ber.*, 1914, **47**, 2565; *A.*, i, 382.

⁴⁹ A. W. Thomas, *Biochem. Bull.*, 1914, **3**, 403; *A.*, i, 6.

⁵⁰ *Zeitsch. physiol. Chem.*, 1915, **93**, 316, 339; **94**, 10; *A.*, i, 325, 326, 653.

on enzymes. It must be admitted, however, that the experimental details are by no means convincing, and it is perhaps sufficient at this stage merely to call attention to the work.

Acids and their Derivatives.

Standard methods of preparing the simpler aliphatic acids are at the present time gradually giving place to processes which depend on catalytic effects, and numerous instances might be quoted to illustrate this point. The methods referred to are, however, generally described in patent literature and present no theoretical novelties, although it is interesting to note that, in the particular case of the catalytic oxidation of acetaldehyde to acetic acid, manganese compounds are extremely efficient agents which work smoothly without the use of oxygen under pressure. This efficiency of manganese salts in oxidation processes is a development which was only to be expected, and deserves wide recognition and use. Among other compounds which may ultimately be utilised in working methods for oxidising aldehydes to acids are the simple organic per-acids, the examination of which has recently been considerably extended,⁵¹ but, on the whole, no strictly novel preparations or reactions involving aliphatic acids have been noted.

Optical Activity.

As in last year's Report considerable space was devoted to optical activity, it is perhaps undesirable that the subject should be so fully dealt with on this occasion. Several valuable and suggestive papers bearing on this topic have, however, appeared during the year, and as the compounds involved are for the most part acids or their simple derivatives, it is most conveniently dealt with at this stage. Practical advantage has been taken of the scheme by means of which the configurations of the active lactic and glyceric acids were determined,⁵² in that Abderhalden is now in a position to assign a definite configuration to *d*-epibromohydrin in virtue of its conversion into *l*-glyceric acid.⁵³ The various steps in the transformation are shown below, not so much with the assurance that the configurations involved are established in these changes, but as examples of reactions which open up a route to the synthesis of optically active fats and similar derivatives.⁵⁴

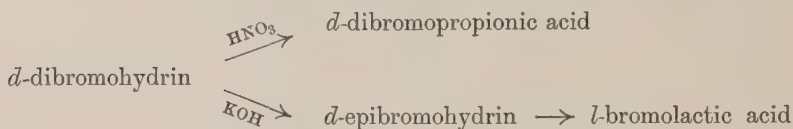
⁵¹ J. D'Ans and A. Kneip, *Ber.*, 1915, 48, 1136; *A.*, i, 769.

⁵² *Ann. Report*, 1914, 65.

⁵³ E. Abderhalden and E. Eichwald, *Ber.*, 1915, 48, 113; *A.*, i, 115.

⁵⁴ *Ibid.*, 2880; *A.*, i, 210.

Allylamine $\rightarrow$ $\alpha\beta$ -dibromoaminopropane $\rightarrow$ d -dibromohydrin
(bromine.) (resolved by tartaric acid.) (nitrous acid.)



Evidently most of the above reactions were complicated by extensive racemisation and the possibility of inversion is very great, but inspection of the scheme shows that a number of important reagents are now available in active forms, and these should add materially to the resources of the synthetical chemist. At the same time it may be remarked that the reactions of epichlorohydrin and epibromohydrin are frequently complex, and the applications of these compounds fall short of what might reasonably be expected from consideration of the highly reactive groups present in the molecules. Additional examples of such irregularities are furnished by the varied action of Grignard reagents on these compounds, and it may be well, at this stage, to call attention once more to the fact.⁵⁵

An advance of a more fundamental nature is the realisation of the idea that optical resolution may take place when an inactive compound is crystallised from an active solvent.⁵⁶ This result was obtained in the course of a research the object of which, equally fundamental in its nature, was to resolve an inactive acid by combination with another active acid in place of a base. On adding a molecular proportion of *l*-malic acid to a solution of potassium racemate, crystals having the composition of potassium hydrogen racemate separated. The product was, however, dextrorotatory owing to the presence of a salt of *d*-tartaric acid. Alteration of the conditions showed this result to be invariable. Again, when potassium hydrogen racemate was dissolved in a hot aqueous solution of *l*-malic acid and the liquid cooled, the material which separated, although consisting essentially of unaltered racemate, was distinctly dextrorotatory, and thus contained some potassium hydrogen *d*-tartrate. There is a peculiar satisfaction in the fact that these results were obtained with compounds which have played an important part in the history of optical activity, and the development of the research will be awaited with much interest.

From studies of resolution it is but a step to the consideration of racemisation and the Walden inversion, and it is significant that many publications deal with the latter type of problem.

⁵⁵ S. I. Iocitsch, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 6; *A.*, 1914, **i**, 375.

⁵⁶ A. McKenzie, *T.*, 1915, **107**, 440; *A.*, **i**, 380.

Attention may be drawn to a suggestive paper,⁵⁷ in which it is shown that active phenyl-*p*-tolylacetic acid is much more prone to racemisation than mandelic acid. This at once shows that the attachment of carbonyl and hydroxyl to the asymmetric atom does not of necessity result in extreme optical instability, and that the lability of a hydrogen atom is probably the responsible agent in such cases of racemisation.

This may be explained in various ways, the simplest view being that a purely desmotropic change of the following nature takes place:



but in order to accommodate the effect of catalysts, the authors make the further suggestion that an unstable additive compound is first formed. The possible transformations of this complex are fully discussed in the original paper, and afford not only a satisfactory explanation of this special type of racemisation, but a reminder to the synthetical chemist that the carboxyl group is by no means so simple as is generally supposed. The whole question of the mechanism of addition to unsaturated molecules is evidently one which still requires extensive research, and the suggestion that these reactions take place in three distinct stages should not be ignored.⁵⁸

In an important study of racemisation,⁵⁹ recently contributed, some highly novel results are described which add a new feature of complexity to the change. Optically active *l*-phenylbromoacetic acid reacts readily with water, and, as in the case of the corresponding chloro-compound, the hydroxylation is accompanied by extensive racemisation, and results initially in the formation of a mixture of *r*- and *l*-mandelic acids. This does not, however, mark the end of the reaction in this particular instance, as the optical rotation gradually assumes a positive value owing to the ultimate formation of a slight excess of the *d*-acid. Not only so, but, particularly when aqueous acetone is used as the solvent, the racemisation is complete before the halogen has been entirely displaced from the bromo-acid. Several factors might contribute to these results, but, of various alternatives, it is difficult to find an explanation which is more satisfactory than that put forward by the authors, who suggest that the following consecutive reactions take place:

⁵⁷ A. McKenzie and Miss S. T. Widdows, *T.*, 1915, **107**, 702; *A.*, i, 814.

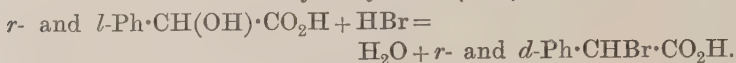
⁵⁸ S. Reich, *J. pr. Chem.*, 1914, [ii], **90**, 177; *A.*, i, 206.

⁵⁹ A. McKenzie and Miss N. Walker, *T.*, 1915, **107**, 1685,

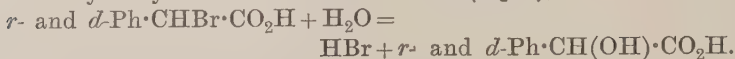
I. Hydroxylation of the *l*-bromo-acid (rapid),



II. Bromination of the hydroxy-acids (slow),

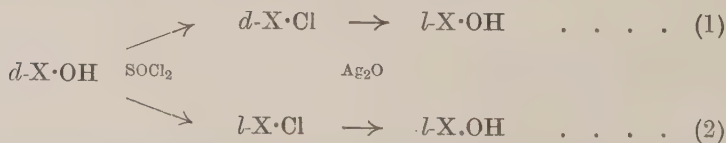


III. Hydroxylation of the bromo-acids (rapid),



A new feature in the study of the Walden inversion is marked by an attack on the problem from the physical point of view, in which the influence of the solvent in affecting the change is taken into account. That the effect of the solvent is considerable was only to be expected, but the fact that in acetonitrile the results may be the opposite of those obtained in aqueous solution emphasises once more the difficulties which accompany all transformations of optically active compounds.⁶⁰ The importance of taking the effect of the solvent into account is further enforced by the evidence, now available, that, in the particular case of the conversion of phenylchloroacetic acid into mandelic acid, the hydrolysis is essentially due to the action of the solvent water on the anion.⁶¹

Although the individual effect of reagents in promoting optical inversions remains to a large extent obscure, and apparently irregular, some definite generalisations have been developed in the course of the voluminous work on this subject. One example of such regularity is the fact that when thionyl chloride and silver oxide are used successively to substitute and regenerate a hydroxyl group, the process always results in inversion. In view of this uniformity, the changes may proceed according to either of the two alternative routes shown below:



where X denotes the part of the molecule attached to the group undergoing substitution. No attempt is made in this scheme to allocate an inversion effect to the individual reagents, as the generalisation extends only to their successive action. As is well known, active lactic acid has been the subject of considerable

⁶⁰ G. Senter and H. D. K. Drew, *T.*, 1915, **107**, 638; *A.*, i, 535.

⁶¹ G. Senter, *T.*, 1915, **107**, 908; *A.*, ii, 538.

attention in this type of inquiry, and it has now been shown⁶² that, in its behaviour towards the above reagents, the compound undergoes inversion according to the second scheme. This adds another example to the list of cases which show that reactions of the type (2) occur only when an alkyl group is attached to the asymmetric carbon atom. In the same paper a suggestive comparison is made of the action of phosphorus pentachloride and thionyl chloride as chlorinating agents, and a description is given of the isolation of intermediate sulphonyl chlorides from both lactic acid and ethyl lactate. In view of Fischer's recent work on a related subject, intermediate compounds of this description assume a new interest.

It is probably as much the duty of the writer of this Report to give his opinion of results which appear to him to be misleading as to direct attention to genuine advances, and, in this connexion, some criticism must be applied to Erlenmeyer's work, to which reference was made last year with some diffidence. The important claim that benzaldehyde can be "activated" by treatment with *d*-tartaric acid seems, on closer inspection, to be baseless, and evidence is now forthcoming, from the originator of the theory of asymmetric induction, that such is the case. The fact, which might in the light of recent work have been foreseen, that benzaldehyde condenses with tartaric acid to give benzylidene-dioxysuccinic acid which is partly esterified, doubtless affords the clue to the existence of "active" benzaldehyde. These benzylidene derivatives are generally highly active and, in this particular case, are laevorotatory.⁶³ They are also very soluble in benzaldehyde, and the fact that the "active" specimen of the aldehyde was not distilled justifies any adverse criticism which may be made against Erlenmeyer's claims.⁶⁴

A considerable amount of experimental work of a highly important nature has recently been carried out on tartaric acid derivatives in continuation of previous studies on rotatory dispersive power and optical superposition, but the detailed consideration of the results would involve overlapping with other sections of the Report, and is thus omitted. Attention may, however, at this stage be directed to a useful practical application which may be made of the effect of different solvents in altering the rotation of a dissolved substance. This effect was first applied by Patterson to discriminate between compounds of closely related structure, and may be used in the measurement of reaction veloci-

⁶² P. F. Frankland and W. E. Garner, *T.*, 1914, 105, 1101.

⁶³ E. Erlenmeyer and G. Hilgendorf, *Biochem. Zeitsch.*, 1914, 68, 351; *A.*, i, 408.

⁶⁴ E. Wedekind, *Ber.*, 1914, 47, 3172; *A.*, i, 256.

ties. In a recent study of the rotation of ethyl tartrate in solution, the optical effect of isomeric or similarly constituted solvents has been ascertained.⁶⁵ The results are striking, and indicate that ethyl tartrate is a suitable and sensitive medium for use in this optical method of settling questions of structure, and its application is probably unaffected by the observation that it is an extremely difficult matter to obtain ethyl tartrate in an optically homogeneous condition.

Halogen Compounds.

Nothing need be said under this heading, as a careful scrutiny of published papers has failed to reveal any reaction or theoretical discussion which would make a general appeal. The Grignard reaction still continues to attract workers, but the problems attacked belong more particularly to the second section of this Report, and have generally been developed on standard lines, although the list of "abnormal" results steadily grows in length and complexity. Oxalyl chloride likewise continues to be a popular reagent, but, in this case also, there are no results which seem to call for special mention.

Nitrogen Compounds.

Diversity of opinion may well prevail as to the precise nature of the nitrogen compounds that may be appropriately discussed in this part of the Report, and, to avoid overlapping with other sections, it will be well to adhere to recent practice and to limit consideration, as far as possible, to compounds which are essentially open-chain structures. Adopting this principle, the more important subjects described in numerous and, in many cases, lengthy papers which have recently appeared fall roughly into three classes.

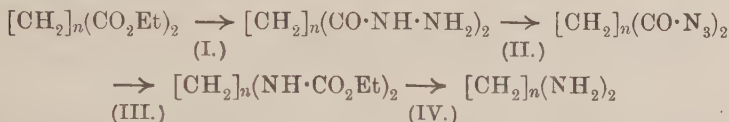
Reactions of Simple Nitrogen Compounds.—The use of amino-compounds of simple type as reagents in condensation reactions is so widely spread that, in all probability, some importance may ultimately be attached to the successful preparation of methylenediamine in the free state, as the result of a series of reactions which do not appear to be unduly difficult.⁶⁶ By the condensation of formamide with formaldehyde, diformomethylenediamide may be produced in good yield, and this, on hydrolysis with hydrochloric acid, is easily converted into the dihydrochloride of methylenediamine:



⁶⁵ T. S. Patterson and E. F. Pollock, *T.*, 1914, **105**, 2322.

⁶⁶ P. Knudsen, *Ber.*, 1914, **47**, 2698; *A.*, i, 220.

The free base, which is unstable, was only isolated in solution, and, although comparatively few of its reactions are described, many possible applications of the compound will at once suggest themselves now that it is readily accessible. The higher homologous diamines display a great variety of reactions, and their preparation by a new method has been rendered available in the course of the systematic work carried out by Curtius on the hydrazides and azoimides of acids belonging to the succinic acid series.⁶⁷ By application of the scheme shown below, the esters of adipic and pimelic acids were respectively converted into tetra- and penta-methylenediamines, the reactions being also applicable to cyclic dibasic acids:



The only noteworthy reaction in the above series is the transformation of the diazoimide into the dicarbamate (stage III), but this change, which is easily effected by heating in alcoholic solution, is simply due to addition of two molecules of the solvent and elimination of two molecules of nitrogen, followed by rearrangement according to recognised principles.

In another paper, which deserves careful study, the question of the structure of aldehyde-ammonia is once more raised and answered in a manner which will at least facilitate the task of the teacher in dealing with this reaction. The formula for acetaldehyde-ammonia suggested by Delépine represented the compound as the trihydrate of trimethylhexahydrotriazine,



but in a research the original object of which was to isolate the compound in the geometric isomerides demanded by this formula, evidence has been obtained which leads to quite different views.⁶⁸ Working with a specially pure preparation of the compound, the molecular weight, determined by the cryoscopic method in aqueous solution, is initially in agreement with the formula $(\text{C}_2\text{H}_7\text{ON})_3$, but the value diminishes until it corresponds with that required for $(\text{C}_2\text{H}_7\text{ON})_2$. This easy degradation from a trimeride to a dimeride is opposed to Delépine's formula, which represents a stable ring structure, and the suggestion is therefore made that the acetaldehyde-ammonias consist of two or more of the above

⁶⁷ T. Curtius, *J. pr. Chem.*, 1915, [ii], **91**, 1; *A.*, i, 124.

⁶⁸ O. Aschan and Y. Vaskio, *Ber.*, 1915, **48**, 874; *A.*, i, 648.

residues linked through nitrogen. According to this view, the trimeride may be regarded as:

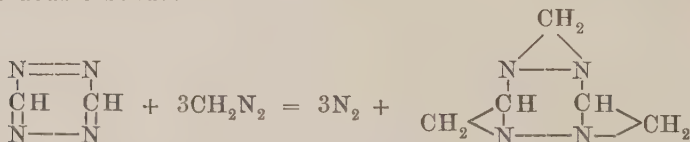


and this, in aqueous solution, gradually undergoes molecular rupture as indicated at the dotted line, being thereby converted into the dimeride:

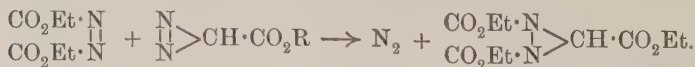


It is interesting to observe that chloral-ammonia loses ammonia spontaneously, giving rise to a product analogous to the above dimeride, and, at the same time, gives dihydroxybistrichloroethylideneimine, $\text{NH}[\text{CH}(\text{OH}) \cdot \text{CCl}_3]_2$, the structure of which is comparable with that of "benzaldehyde-ammonia."

Considering the value of diazomethane as a reagent, all unexpected reactions of the compound are specially important, and attention should be directed to the irregular result to which it gives rise in the case of 1:2:4:5-tetrazine.⁶⁹ In place of yielding a dimethyltetrazine, the reaction involves three molecules of diazomethane and the consequent addition of three methylene groups at the double bonds:



Apparently the above type of reaction is capable of considerable variation, as ethyl diazoacetate behaves in a similar manner towards ethyl azodicarboxylate, in this case a substituted methylene group becoming attached to the nitrogen atoms with the formation of an authentic derivative of hydraziacetic acid.

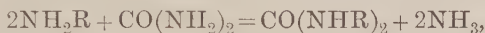


Carbamides.—It is somewhat surprising to find that reactions involving the use of carbamide at comparatively high temperatures still continue to attract workers. Naturally enough, it is difficult to disentangle any generalisations from the results thus obtained or to find good reasons for the selection of reacting materials. Among the simpler of these reactions is the observation that, at a temperature of 170°, carbamide and acetophenone enter into symmetrical condensation to give $\text{CPhMe} \cdot \text{N} \cdot \text{CO} \cdot \text{N} \cdot \text{CPhMe}$, but, on the other hand, under similar conditions ethyl acetoacetate occasions

⁶⁹ E. Müller, *Ber.*, 1914, **47**, 3001; *A.*, i, 509.

a reaction of greater complexity.⁷⁰ In this case, a molecule of alcohol is lost and the potential ketonic group enters into condensation with two molecules of the carbamide. Speculation as to the possible progress of this reaction must be at least empirical, and is best avoided. The same criticism applies to the observation that carbamide sometimes reacts with unsaturated esters to give the amino-ester where the action of ammonia results in the formation of the acid amide.⁷¹ In such cases it is obviously not the carbamide as such which reacts, but its decomposition products, and these only come into operation at a temperature at which amide-formation is extremely slow or entirely suspended.

A method for the preparation of symmetrically substituted carbamides which, although somewhat restricted in scope, will nevertheless be useful in many ways, consists in the direct reaction of a carbamide with a primary amine in the presence of acetic acid. The normal change is the formation of a symmetrical dialkyl-carbamide according to the scheme



but starting from a monoalkylcarbamide and using an amine with a different alkyl group it is possible to obtain derivatives where R and R₁ are unlike.⁷² Inspection of the original paper gives the impression that the experimental methods employed are by no means difficult and may be developed into satisfactory processes.

Evidently all the reactions of carbamide have to be viewed in terms of more than one formula for the compound, and indirect evidence in favour of the cyclic structure $\text{NH}:\text{C} \begin{smallmatrix} \nearrow \text{NH}_3 \\ \searrow \text{O} \end{smallmatrix}$ is quoted in the course of a discussion on the constitution of cyanamide.⁷³ In order to explain the stability of this compound, and above all its polymerisation by both acids and alkalis, the suggestion is made that it exists in aqueous solution as an equilibrium mixture of acidic and basic forms.



On this basis, the different routes followed in the auto-condensation of the compound receive a ready explanation, as in the presence of acid and alkali respectively the basic and acidic forms are removed from the system, and two different types of molecular rearrangement thus come into operation.

⁷⁰ M. Scholtz, *Arch. Pharm.*, 1915, **253**, 111; *A.*, i, 846.

⁷¹ E. Philippi and E. Spenner, *Monatsh.*, 1915, **36**, 97; *A.*, i, 222.

⁷² A. Sonn, *Ber.*, 1914, **47**, 2437; *A.*, i, 394.

⁷³ E. A. Werner, *T.*, 1915, **107**, 715; *A.*, i, 784.

Acid polymerisation—basic form removed.



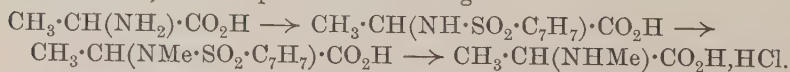
Alkaline polymerisation—acidic form removed.



These ideas serve to explain a number of the reactions of cyanamide, including the fact that nitrous acid acts on the compound at first vigorously and thereafter only slowly, the assumption being that the initial action disposes of the free amino-form and that the subsequent formation of this variety, owing to the readjustment of equilibrium in the system, is slow. Again, the remarkable reluctance with which cyanamide adds on the elements of water points to the idea that carbamide and cyanamide are not simply related, and that the open-chain structure for the former compound is thus not universally applicable.

Amino-acids.—As the result of several recent researches, a distinct advance has been made in the experimental treatment of optically active amino-acids, as it is now possible to obtain the methyl homologues of these compounds without danger of racemisation or the risk of losing trace of the configuration in virtue of Walden inversions taking place. These difficulties, in addition to others, attended the older methods of preparation, in which the corresponding active bromo-acids were decomposed with methylamine, and are overcome by starting the syntheses from the parent amino-acid in an active form. The various steps involved are best illustrated by reference to a particular case, and for this purpose the preparation of *d*-methylalanine from *d*-alanine may be selected.⁷⁴

By the action of *p*-toluenesulphonyl chloride, one hydrogen atom of the amino-group is displaced, and the remaining atom may then be methylated by the joint action of methyl iodide and sodium hydroxide.⁷⁵ In the particular case under consideration, the removal of the arylsulphonyl residue is easily effected by concentrated hydrochloric acid, and takes place without appreciable racemisation, the complete scheme being



In certain cases, however, some trouble was experienced in decom-

⁷⁴ E. Fischer and W. Lipschitz, *Ber.*, 1915, **48**, 360; *A.*, i, 242.

⁷⁵ E. Fischer and M. Bergmann, *Annalen*, 1913, **398**, 96; *A.*, 1913, i, 710.

posing the arylsulphonyl derivatives, but this was overcome by the use of hydriodic acid and phosphonium iodide. A noteworthy example involving the application of this joint reagent is the conversion of *l*-tyrosine into *N*-methyltyrosine, which has been proved to be identical with natural rhatanin.⁷⁶ The above general method will doubtless be applicable even in cases where the parent amino-acid is not readily available in an active form as the equilibrium method of resolving inactive acids, first applied successfully to benzoylalanine,⁷⁷ is capable of resolving inactive *p*-toluenesulphonylalanine with an accuracy equal to that attained by Fischer in the first stage of the scheme illustrated above.⁷⁸

Other work relating to amino-acids is less definite in character, and is largely concerned with the capacity of these compounds to form anhydrides under conditions which appear to be so drastic that all speculation as to the mechanism of the changes involved is excluded. Some dubiety still exists⁷⁹ as to the part played by glycerol in promoting the different types of anhydride formation, but the essential facts recorded are simple. In a lengthy paper the conversion of a number of amino-acids into cyclic anhydrides by heating with glycerol is described, and as the compounds which resulted are already known, it is possible to form an approximate idea of the reactions involved. The changes were accompanied by secondary reactions, and it is not surprising that only racemic products resulted.⁸⁰ In a more detailed study of the same problem it has been shown⁸¹ that the first product formed is the *cyclo*-anhydride, followed on continued action by open-chain compounds, the formation of which is, however, attended by decomposition. In the original paper the supposed function of the glycerol in promoting these changes is explained by an ingenious structural scheme which, in view of the claim that the reactions are comparable with those resulting in the natural formation of proteins, deserves mention.

It would be undesirable to close this section of the Report without reference to new observations which have a bearing on the formation of internal salts from amino-acids. The work was carried out with cyclic acids, the evidence of ring-formation being based on changes in optical activity, and leads to the conclusion that salts of the type $\text{H} \begin{array}{c} \text{CO}^- \\ \diagup \quad \diagdown \\ \text{NH}_3 \end{array} \text{O}$ can exist in aqueous solution

⁷⁶ E. Fischer, *Ber.*, 1915, **48**, 93; *A.*, i, 138.

⁷⁷ W. J. Pope and C. S. Gibson, *T.*, 1912, **101**, 939.

⁷⁸ C. S. Gibson, *P.*, 1914, **30**, 32.

⁷⁹ F. Graziani, *Atti R. Accad. Lincei*, 1915, [v], **24**, i, 822, 936; *A.*, i, 781, 869.

⁸⁰ L. C. Maillard, *Ann. Chim.*, 1915, [ix], **3**, 48; *A.*, i, 462.

⁸¹ *Ibid.*, 1914, [ix], **2**, 210; *A.*, i, 121.

when the ring produced contains as many as six atoms.⁸² On the other hand, no such cyclic structure containing seven or more atoms is formed, the open-chain, $\text{NH}_2 \cdot \text{R} \cdot \text{CO}_2\text{H}$, then persisting. The work referred to is interesting as a good example of the use of the polarimeter in the study of constitution and in furnishing striking examples of the optical effects which accompany ring-formation.

JAMES COLQUHOUN IRVINE.

PART II.—HOMOCYCLIC DIVISION.

THERE has been no lack of material for this section of the Annual Report this year, for the output of work generally has been fairly well maintained, and rather more than a year's supply of German and Austrian periodicals has become available. Attention may be directed to H. S. Fry's electronic formula for benzene,¹ which has been recently discussed at considerable length by its author, and criticised by A. F. Holleman² and R. F. Brunel.³ The subject is not, however, suitable for condensation into a small space, and the original papers should be consulted.

Reactions.

Nitration.—Last year it was mentioned⁴ that of the six possible trinitro-derivatives of toluene only three were known, namely, the commercial product which is 2:4:6-trinitrotoluene, and the 2:3:4- and 2:4:5-trinitrotoluenes. The 3:4:5- and 2:3:5-derivatives have now been prepared by decomposing the diazonium nitrates derived from 3:5-dinitro-*p*- and *o*-toluidines respectively with sodium nitrite,⁵ and a sixth isomeride, which can only be the 2:3:6-derivative, has been isolated from the products of nitration of toluene.⁶ Several interesting papers deal with the relative

⁸² W. A. Noyes and R. S. Potter, *J. Amer. Chem. Soc.*, 1915, **37**, 189; *A.*, i, 79.

¹ *Zeitsch. physikal. Chem.*, 1911, **76**, 385, 398, 591; *J. Amer. Chem. Soc.*, 1914, **36**, 248, 262, 1035; 1915, **37**, 855, 2368; *A.*, 1911, i, 431; 1914, i, 263, 675; 1915, i, 391; ii, 760.

² *ibid.*, 1914, **36**, 2495; *A.*, i, 9.

³ *ibid.*, 1915, **37**, 709; *A.*, ii, 332.

⁴ *Ann. Report*, 1914, 99.

⁵ W. Körner and A. Contardi, *Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 464; 1915, [v], **24**, i, 888; *A.*, i, 875, 790.

⁶ E. Molinari and M. Giua, *Zeitsch. ges. Schiess-Sprengstoff-wesen*, 1914, **9**, 239; *A.*, i, 790.

directing influence of substituents in the benzene nucleus on the position taken up by an entering nitro-group, and others with the influence of nitro-groups on the elimination of substituents from a substituted nitrobenzene. A study of the nitration of mixed dihalogenobenzenes to mononitro-derivatives leads to the following results.⁷ In *o*-chlorobromobenzene the substitution velocities caused by chlorine and bromine have the ratio $\text{Cl} : \text{Br} = 1 : 0.8$. In the case of *o*-chloriodobenzene the ratio is $\text{Cl} : \text{I} = 1 : 1.84$. By calculation, then, the ratio in the case of *o*-bromiodobenzene should be $\text{Br} : \text{I} = 1 : 2.30$. As the result of experiment, however, it is found to be $1 : 1.75$, and it would, therefore, seem that the two substituents modify each other's properties, but the results are not exact, for it is impossible to estimate exactly the error due to the elimination of iodine from the iodo-substituted benzenes.

In *p*-chlorobromobenzene the relative velocity of substitution caused by the two halogens is $\text{Cl} : \text{Br} = 1 : 0.96$, a ratio differing from that found in the case of the ortho-substituted derivative. Nitration of *p*-bromotoluene gives a mixture of 4:2- and 4:3-bromonitrotoluenes, in which the former predominates.⁸

3-Chloro-5-bromotoluene, which contains three different substituents symmetrically arranged in the nucleus, gives a mono-, di-, and tri-nitro-derivative, all of which are apparently homogeneous. The first nitro-group to enter takes up the position between the methyl group and the bromine atom, whilst the second most probably enters the position between the methyl group and the chlorine atom.⁹

Aniline when nitrated in concentrated sulphuric acid solution gives a considerable proportion of *m*-nitroaniline. Anilides such as acetanilide, however, give only the ortho- and para-nitro-derivatives. The question, therefore, arose as to how the anilides of stronger acids would behave, and the nitration of the anilides of mono-, di-, and tri-chloroacetic acid has been studied. These anilides yield solely ortho- and para-substituted nitro-derivatives, even when nitrated in concentrated sulphuric acid solution. It is not, therefore, the combination of the amino-group with a strong acid that causes aniline in concentrated sulphuric acid to yield *m*-nitroaniline, but possibly a meta-directing influence of the ammonium salt grouping.¹⁰

When trinitro- ψ -cumene is heated with alcoholic ammonia, the 6-nitro-group is readily displaced, 3:5-dinitro-6- ψ -cumidine (I) being

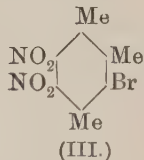
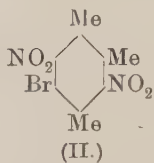
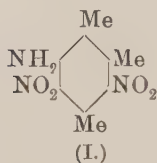
⁷ A. F. Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 846; *Rec. trav. chim.*, 1915, **34**, 204; *A.*, i, 59, 659.

⁸ A. F. Holleman, *ibid.*, 283; *A.*, i, 875.

⁹ J. B. Cohen and W. J. Murray, *T.*, 1915, **107**, 847; *A.*, 791.

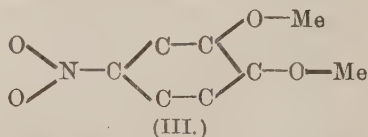
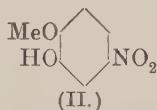
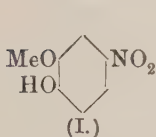
¹⁰ E. Votoček and J. Burda, *Ber.*, 1915, **48**, 1002; *A.*, i, 662.

formed. The latter substance is only obtained with difficulty from 6-chloro-3:5-dinitro- ψ -cumene, and cannot be obtained from 6-bromo-3:5-dinitro- ψ -cumene. In 5-bromo-3:6-dinitro- ψ -cumene (II)



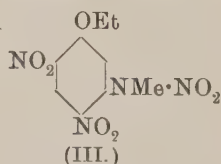
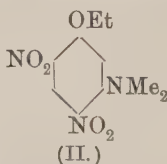
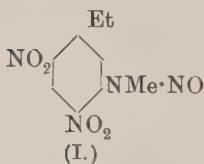
neither the bromine atom nor the 6-nitro-group is readily displaced by the amino-group, and in 3-bromo-5:6-dinitro- ψ -cumene (III) similar displacement cannot be effected.¹¹

Nitroveratrole is hydrolysed to 4-nitroguaiacol (I) by alkaline reagents and to 5-nitroguaiacol (II) by acids. This interesting result receives an explanation in the light of the theories of Werner and Flürscheim. The distribution of affinity in nitroveratrole is shown in III, in which the thickened lines represent strengthened affinities, and it will be seen that the point of attack for hydroxyl



ions would be at the para-positions with respect to the nitro-group, whilst the methyl group of the meta-methoxy-group would be the more likely to be removed by means of hydrogen ions.¹²

Nitration of dimethyl-*m*-phenetidine at 70° yields 4:6-dinitro-3-nitrosomethylaminophenetole (I), and at 25° a mixture of this substance with 4:6-dinitro-3-dimethylaminophenetole (II). Both the original base and the nitrosoamine give 4:6-dinitro-3-methylnitroaminophenetole (III) when nitrated in acetic anhydride solution. Similar series of compounds were obtained by the nitra-



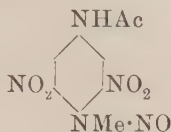
tion of dimethyl-*m*-anisidine and diethyl-*m*-phenetidine.¹³ It is particularly interesting to note that compounds of the type (*p*) $\text{AcNH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMeR}$, where $\text{R} = \text{Me, Et, or Bz}$, all give on nitration

¹¹ A. Huender, *Rec. trav. chim.*, 1915, **34**, 1; *A.*, i, 129.

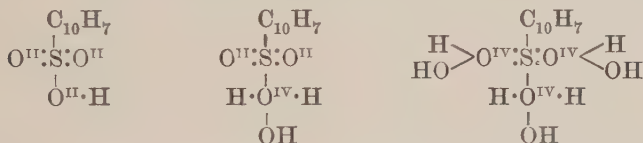
¹² D. Cardwell and R. Robinson, *T.*, 1915, **107**, 255; *A.*, i, 134.

¹³ F. Reverdin, *Bull. Soc. chim.*, 1915, [iv], **17**, 190, 278; *A.*, i, 524, 878.

the same product, formulated below, R being expelled, and replaced by the nitroso-group.¹⁴



Sulphonation.—Although the naphthalenesulphonic acids are most important substances in the dye industry, the published information as to their properties is incomplete, and not wholly accurate. An interesting paper on the preparation and properties of naphthalene- β -sulphonic acid has recently appeared.¹⁵ This acid is readily obtained by the sulphonation of naphthalene with concentrated sulphuric acid (93·7 per cent.) at 160°, and is freed from the small proportion of the α -isomeride, formed at the same time, by the crystallisation of its trihydrate. Naphthalene- β -sulphonic acid forms a well-defined monohydrate also, and it is shown that several of the salts lose their water of crystallisation in two steps corresponding with these two hydrates. The author suggests that the oxygen atoms of the sulphonic acid grouping are “infected” by the sexavalent sulphur atom of this group, with an inclination to multivalency and become quadrivalent. This view leads to the following formulæ for the anhydrous acid and the two hydrates:



The effect of aqueous alkalis on sulphonic acids at high temperatures has been studied. Benzenesulphonic acid is only slowly attacked by 10 per cent. sodium hydroxide at 320°, but the naphthalenesulphonic acids readily give good yields of the pure naphthols.¹⁶ The position is reversed in the preparation of the hydroxy-derivatives from the chloro-hydrocarbons, for in this case chlorobenzene is smoothly converted into phenol by 15–20 per cent. aqueous sodium hydroxide at 300°, whilst α -chloronaphthalene only slowly gives a moderately good yield of α -naphthol.¹⁷ In methyl-alcoholic solution, however, a good yield of α -naphthol from α -chloronaphthalene is obtained.¹⁸

¹⁴ R. Meldola and W. F. Hollely, *T.*, 1915, **107**, 610; *A.*, i, 587.

¹⁵ O. N. Witt, *Ber.*, 1915, **48**, 743; *A.*, i, 515.

¹⁶ K. H. Meyer and F. Willson, *ibid.*, 1914, **47**, 3160; *A.*, i, 232.

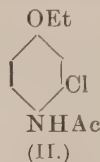
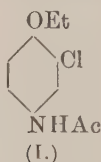
¹⁷ K. H. Meyer and F. Bergius, *ibid.*, 3155; *A.*, i, 231.

¹⁸ D. R.-P., 281175; *A.*, i, 674.

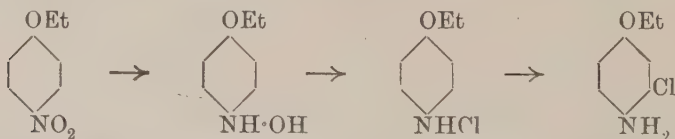
Chlorination.—Comparison of the directing influences of various groups in the chlorination of aromatic compounds shows that the amino-group far surpasses all others, and is followed by the groups hydroxyl, alkoxyl, and acetamino in this order¹⁹:



The chlorination of phenacetin, which contains the two latter groups, by hypochlorous acid,²⁰ or by chlorine evolved from a chloroamine and hydrochloric acid,²¹ gives a product which consists largely of 2-chloroaceto-*p*-phenetidine (I). The isomeric 3-chloro-



aceto-*p*-phenetidine (II) is obtained by the acetylation of 3-chloro-*p*-phenetidine. This substance is obtained in a yield of 90 per cent. of the theoretical by the reduction of *p*-nitrophenetole with tin and hydrochloric acid.²² The formation of by-products containing chlorine has frequently been observed in the reduction of aromatic nitro-compounds to amino-compounds in this manner, and is probably due to the intermediate formation of aryl-hydroxylamines and chloroamines,²³ which can be represented in the present case as follows:



The fact that 3-chloro-*p*-phenetidine is obtained in this manner unaccompanied by 2-chloro-*p*-phenetidine may well be due to the greatly superior directing influence of the amino-group to that of the ethoxy-group.

It is interesting to note that whilst 2-nitroresorcinol dimethyl ether gave a mixture of 2-aminoresorcinol dimethyl ether, and a chloro-2-aminoresorcinol dimethyl ether on reduction with tin and

¹⁹ F. S. Kipping, K. J. P. Orton, S. Ruhemann, and J. T. Hewitt, *Brit. Assoc. Report*, 1915; *Chem. News*, 1915, **112**, 152.

²⁰ F. Reverdin and F. Düring, *Ber.*, 1899, **32**, 152; *A.*, 1899, i, 266.

²¹ K. J. P. Orton and H. King, *T.*, 1911, **99**, 1190; compare Miss W. G. Hurst and J. F. Thorpe, *ibid.*, 1915, **107**, 934; *A.*, i, 797.

²² Miss W. G. Hurst and J. F. Thorpe, *loc. cit.*

²³ E. Bamberger, *Ber.*, 1895, **28**, 245; S. Gabriel and R. Stelzner, *Ber.*, 1896, **29**, 303; *A.*, 1895, i, 217; 1896, i, 320.

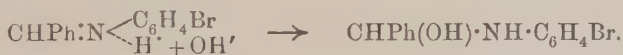
hydrochloric acid, the formation of a chlorinated by-product in the reduction of 2-nitroresorcinol diethyl ether does not appear to have been observed.²⁴

Bromination.—The bromination of aromatic amines by a solution of bromine in acetic acid tends to give rise, with meta-substituted anilines and aniline itself, to tribromo-derivatives; with ortho- and para-substituted anilines, to dibromo-derivatives. The amino-group is of greater directive influence than any other group tested; thus *p*-toluidine, acetyl-*p*-phenylenediamine, and *p*-phenetidine all give 2:6-dibromo-anilines.²⁵

When benzyldeneaniline dibromide is heated with absolute alcohol, benzyldene-*p*-bromoaniline hydrobromide is formed. A. Hantzsch and O. Schwab²⁶ formulated the hydrobromide as a true salt, $C_6H_4Br \cdot N \cdot CHPh \cdot HBr$, in spite of the fact that it yields benzaldehydo-*p*-bromoaniline, $C_6H_4Br \cdot NH \cdot CHPh \cdot OH$, when heated with aqueous sodium carbonate. The alternative formula,



which these authors rejected, has been supported during the year by H. Frauzen and A. Henglein,²⁷ but on insufficient grounds, as Hantzsch²⁸ has clearly shown; for the salts of Schiff's bases are insoluble in ether, and behave physico-chemically as the salts of weak bases; moreover, the hydrochlorides can be converted into platinichlorides. The formation of benzaldehydo-*p*-bromoaniline from benzyldene-*p*-bromoaniline hydrobromide may be an instance of pseudo-base formation:



Reduction.—The value of the arylsulphonyl derivatives of amino-compounds for the isolation of this class of compound is seriously diminished by the difficulty of regenerating the original amino-compound. Hitherto, concentrated hydrochloric acid at 100° or higher temperatures has been employed for the hydrolysis, a method which frequently gives rise to racemised products in the case of optically active amino-compounds, such as amino-acids. It is now found that arylsulphonamides and their derivatives readily suffer reduction and fission into thiophenols and amino-compounds when heated with fuming hydriodic acid and phosphonium iodide at 70—100°:



²⁴ E. E. Turner, *T.*, 1915, **107**, 469.

²⁵ W. Fuchs, *Monatsh.*, 1915, **36**, 113; *A.*, i, 520.

²⁶ *Ber.*, 1901, **34**, 822; *A.*, 1901, i, 378.

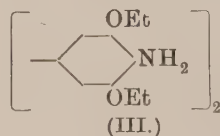
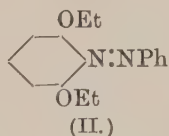
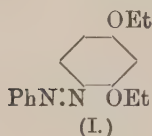
²⁷ *J. pr. Chem.*, 1915, [ii], **91**, 245; *A.*, i, 230.

²⁸ *Ber.*, 1915, **48**, 1340; *A.*, i, 1053.

The method is especially suitable for the recovery of optically active amino-acids from their arylsulphonyl derivatives.

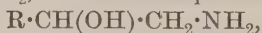
Like the arylsulphonamides, arylsulphonyl chlorides may also be reduced to thiophenols by hydriodic acid, but the free sulphonic acids and their esters cannot be reduced in this way.²⁹ A number of mono- and poly-thiol-benzenes and -naphthalenes have been prepared by the reduction of arylsulphonyl chlorides by zinc or tin and hydrochloric acid.³⁰

4-Benzeneazoresorcinol diethyl ether (I) gives on reduction with alcoholic stannous chloride, 4-aminoresorcinol diethyl ether. The product obtained from 2-benzeneazoresorcinol diethyl ether (II) under the same conditions is not identical with 2-aminoresorcinol diethyl ether, and is probably 4:4'-diamino-3:5:3':5'-tetraethoxydiphenyl (III), since the reducing agent employed is specific for inducing the benzidine change.³¹



Attempts to transform *m*-halogenostyrenes into *m*-halogenoethylbenzenes by catalytic reduction were unsuccessful, for halogen was eliminated, and the corresponding saturated hydrocarbons were obtained. Benzyl chloride, under similar conditions, gives toluene in good yield, benzylidene chlorides gives toluene and a small amount of *s*-dichlorodiphenylethane, $\text{CHClPh} \cdot \text{CHClPh}$, whilst benzotrichloride, PhCCl_3 , gives only *s*-tetrachlorodiphenylethane, $\text{CPhCl}_2 \cdot \text{CPhCl}_2$.³²

Hydrogen and palladinised charcoal reduce aryl aminoalkyl ketones, $\text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$, to the corresponding carbinols,



in good yield, whereas other reducing agents give poor results.³³

Oxidation.—Little is known as to the nature of the oxidation products of polyhydric phenols. Some years ago it was shown that pyrogallol became oxidised by air in the presence of barium hydroxide to 2:3:4:2':3':4'-hexahydroxydiphenyl (I),³⁴ and it is now

²⁹ E. Fischer, *Ber.*, 1915, **48**, 93; *A.*, i, 138.

³⁰ T. Zincke and J. Ruppertsberg, *ibid.*, 120; H. Rennert, *ibid.*, 459; J. Pollak (in part with A. Wienerberger), *Monatsh.*, 1914, **35**, 1445, 1467; *A.*, i, 135, 531, 528, 529.

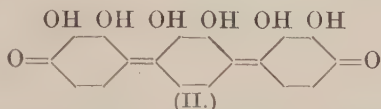
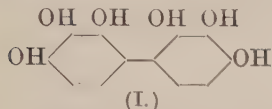
³¹ E. E. Turner, *T.*, 1915, **107**, 469; *A.*, i, 396.

³² W. Borsche and O. Heimbürger. *Ber.*, 1915, **48**, 542; *A.*, i, 527.

³³ C. Mannich and E. Thiele, *Arch. Pharm.*, 1915, **253**, 181; *A.*, i, 812.

³⁴ C. Harries, *Ber.*, 1902, **35**, 2954; *A.*, 1902, i, 771; M. Nierenstein and F. W. Rixon, *Annalen*, 1912, **394**, 249; *A.*, 1913, i, 180.

shown that it yields with air and potassium hydroxide a hexahydroxytriphenoquinone, which appears to have the constitution represented by formula II.³⁵

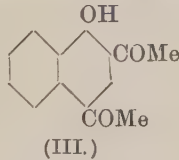
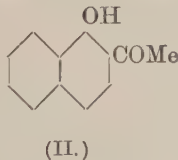
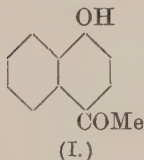


Similarly, orcinol on oxidation with air in aqueous potassium hydroxide gives a crystalline quinone, which yields a triacetate, and probably has the formula $(\text{HO})_2\text{C}_6\text{H}_2\text{Me}\cdot\text{C}_6\text{HMe}(\text{:O})_2\cdot\text{OH}$.³⁶

Resorcinol, when fused with sodium hydroxide, gives, besides phloroglucinol, a quantity of tetrahydroxydiphenyl (diresorcinol). Since the yield of the latter increases at the expense of the yield of phloroglucinol on raising the temperature, it is probable that phloroglucinol is an intermediate product in the formation of diresorcinol. This view supports the constitution usually assigned to the latter substance, where the hydroxyl groups occupy the 3:5:3':5'-positions.³⁷

The earlier results obtained by oxidising phenols containing unsaturated side-chains with strong ozone were unsatisfactory, resinous products being largely formed; when, however, 1 per cent. dry ozone is used, eugenol and isoeugenol yield the normal mono-ozonides, which on reduction with zinc dust and acetic acid in ethereal solution give homovanillin and vanillin respectively in good yield.³⁸

Friedel and Crafts' Reaction.—An instance of intramolecular change has been observed in the hydrolysis of the alkyl ethers of phenol-ketones by Gattermann's method. When 4-ethoxy- α -naphthyl methyl ketone is heated with aluminium chloride in benzene solution, the normal product, 4-hydroxy- α -naphthyl methyl ketone (I) is obtained, but when no diluent is employed, 1-hydroxy- β -naphthyl methyl ketone (II) is produced, together with α -naphthol and the di-substituted derivative (III) under the combined analytic and



synthetic actions of the reagent.

³⁵ M. Nierenstein, *T.*, 1915, 107, 1217; *A.*, i, 883.

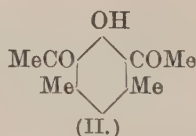
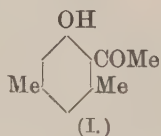
³⁶ F. Henrich, W. Schmidt, and F. Rossteutscher, *Ber.*, 1915, 48, 483; *A.*, i, 564.

³⁷ O. von Friedrichs, *Arkiv Kem. Min. Geol.*, 1914, 5, No. 19, 1; *A.*, i, 811.

³⁸ C. Harries and R. Haarmann, *Ber.*, 1915, 48, 32; *A.*, i, 133.

When α -naphthol is heated with glacial acetic acid and zinc chloride, a 30 per cent. yield of 1-hydroxy- β -naphthyl methyl ketone (II) is obtained. The addition of acetic anhydride to the materials used in the reaction increases the yield to 80 per cent., and this fact suggests that the primary product of the reaction is α -naphthyl acetate, which then suffers rearrangement.³⁹ In the analogous case of phenol, however, neither the addition of acetic anhydride nor the use of ready-made phenyl acetate has a favourable influence on the yield, so that the foregoing explanation is not of general applicability. It may well be that the intermediate product in this synthesis is an organo-metallic derivative, just as is assumed for the Friedel and Crafts' reaction, and it is suggested that the yellow colour produced by the action of zinc chloride on phenol and acetic acid is an indication of the formation of such a compound.⁴⁰

The condensation of *s-m*-xylene methyl ether with acetyl chloride in the presence of aluminium chloride gives a surprising result, for the acetyl group enters the ortho-position to the methoxy-group. Similarly the xylenyl acetate gives the ortho-substituted hydroxy-ketone (I), and as a by-product the diortho-substituted compound (II).⁴¹



The chlorides of anthraquinone-1- and -2-carboxylic acids can be condensed with hydrocarbons by Friedel and Crafts' reaction, giving 1- and 2-benzoylanthraquinones, but the reaction only proceeds smoothly with the compounds of the latter type.⁴² The products differ considerably in their properties, 2-benzoylanthraquinones yielding colourless anthranols on reduction, whilst 1-benzoylanthraquinones give highly coloured substances which are insoluble in sodium hydroxide, and are therefore not anthranols.⁴³

The condensation of phthaloyl chloride with aromatic hydrocarbons in the presence of aluminium chloride leads to a mixture of the corresponding phthaloylic acids and phthalides; thus with *o*-xylene, *o*-xylylphthaloylic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me}_2$, and di-*o*-xylylphthalide, $(\text{C}_6\text{H}_3\text{Me}_2)_2\text{C} < \text{C}_6\text{H}_4 > \text{CO}$, are formed.⁴⁴

³⁹ O. N. Witt and O. Braun, *Ber.*, 1914, **47**, 3216; *A.*, i, 414.

⁴⁰ H. Pauly and K. Lockemann, *ibid.*, 1915, **48**, 28; *A.*, i, 146.

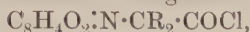
⁴¹ K. v. Auwers, *ibid.*, **90**; *A.*, i, 145.

⁴² A. Schaarschmidt, *ibid.*, 831; *A.*, 566.

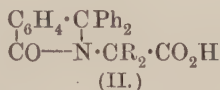
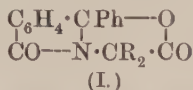
⁴³ A. Schaarschmidt, *ibid.*, 973; *A.*, i, 696.

⁴⁴ M. Copisarow and C. Weizmann, *T.*, 1915, **107**, 878; *A.*, i, 686.

Phthaliminoacetyl chlorides of the general formula,



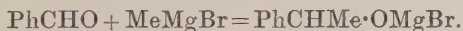
condense with benzene and aluminium chloride to give phthaliminoacetophenones, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{CR}_2\cdot\text{COPh}$, together with by-products (I) and (II) formed by the participation of one of the phthaloyl carbonyl groups in the reaction.⁴⁵



The steric arrangement of the methyl groups in mesitylene permits the introduction of alkyl and acyl groups by means of Friedel and Crafts' reaction, but not that of the esters of halogen-fatty acids, for instance, methyl chloroformate, chloroacetate, or β -iodopropionate.⁴⁶

The Friedel and Crafts and the Nencki methods have a limited scope of application to syntheses of phenolic ketones. An important new method of synthesising these substances, which are closely related to many natural products, is an extension of Gattermann's method of synthesis of phenolic aldehydes from a phenol, hydrocyanic acid, and hydrogen chloride. By the use of a nitrile in the place of the hydrocyanic acid, a ketone-imide hydrochloride of the type $\text{CRR}'\cdot\text{NH}\cdot\text{HCl}$ is formed, and this on hydrolysis yields the ketone $\text{R}\cdot\text{COR}'$. The entering group takes up the para-position with respect to a phenolic hydroxyl group.⁴⁷

Grignard's Reaction.—Magnesium methyl bromide combines with benzaldehyde in equimolecular proportions in ethereal solution to form a crystalline precipitate. On the addition of a second molecular proportion of the aldehyde, the precipitate changes to a viscous mass, which on decomposition with water yields acetophenone and benzyl alcohol:



It is evident that combination takes place between the magnesium phenylmethylcarbinyl bromide and the second molecular proportion of benzaldehyde, for the supernatant ethereal liquor contains only traces of the latter. The view is put forward⁴⁸ that an ortho-compound, $\text{PhC(OMgBr)(O}\cdot\text{CH}_2\text{Ph)Me}$, is formed as an intermediate product. The second molecule of benzaldehyde acts as an

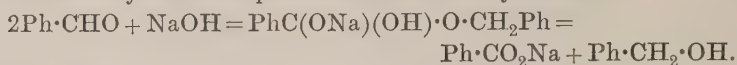
⁴⁵ P. Freytag, *Ber.*, 1915, **48**, 648; *A.*, i, 543.

⁴⁶ F. Wenzel, *Monatsh.*, 1914, **35**, 945; *A.*, i, 541.

⁴⁷ K. Hoesch, *Ber.*, 1915, **48**, 1122; *A.*, i, 820.

⁴⁸ J. Marshall, *T.*, 1915, **107**, 509; *A.*, i, 409.

oxidising agent, itself becoming reduced to benzyl alcohol, a reaction which is very similar to the simultaneous oxidation and reduction of benzaldehyde in the presence of sodium hydroxide.



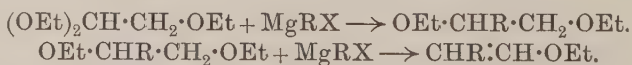
The methyl hydroxytoluates behave normally with the Grignard reagents, giving hydroxytoluoldialkyl-(or aryl)-carbinols,



methyl 2-hydroxy-3-naphthoate behaves similarly,⁵⁰ but methyl 1-hydroxy- β -naphthoate frequently yields ethylene derivatives or naphthaquinones owing to the instability of the tertiary carbinols.⁵¹

The influence of the positions of the halogen and carboxyl groups in the esters of halogenated aromatic acids on the reaction with magnesium is as follows: When both groups are in the side-chain, the compounds react with magnesium; when both are united directly to the nucleus the tendency to react is much diminished; when the halogen is in the nucleus and the carboxyl in the side-chain, the former is rendered slightly more mobile (ethyl *p*-bromophenylacetate does not react, whilst the ortho-compound does so); when the carboxyl is in the nucleus, and the bromine in the side-chain, the esters exhibit increased activity towards magnesium; thus, ethyl ω -bromo-*o*- and *m*-toluates react, forming compounds, $\text{C}_6\text{H}_4\text{Me}\cdot\text{C(OH)(CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H)}_2$, although here also the para-derivative is inactive.⁵²

A useful method of preparing the otherwise difficultly accessible substituted phenylacetaldehydes has been described. Ethoxyacetal reacts with the Grignard reagent to give a mixture of two ethers, thus:



Both ethers are readily hydrolysed by hot 50 per cent. sulphuric acid, giving the same aldehyde, $\text{R}\cdot\text{CH}_2\cdot\text{CHO}$.⁵³

Steric Influence.

The steric effect of substituents on the formation of formanilides from substituted aromatic amines, $\text{C}_6\text{H}_4\text{X}\cdot\text{NH}_2$ (where X = Me, OMe, Cl, or Br), has been studied. In comparing the relative rates of formation (with which the percentage of anilide formed runs

⁴⁹ H. Berlitz, *Monatsh.*, 1915, **36**, 191; *A.*, i, 533.

⁵⁰ P. Lammer, *ibid.*, 1914, **35**, 171; *A.*, 1914, i, 409.

⁵¹ F. Preissecker, *ibid.*, 889; *A.*, i, 525.

⁵² J. Zalkind and A. A. Schmidt, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 681; *A.*, i, 407.

⁵³ E. Späth, *Monatsh.*, 1915, **36**, 1; *A.*, i, 262.

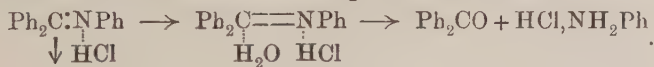
approximately parallel) of the ortho-, meta-, and para-isomerides, the steric hindrance is in the order $o > m > p$. Comparison of the effects of the different groups shows that in the *o*-series the steric influence is in the order $\text{OMe} > \text{Me} > \text{Br} > \text{Cl}$; in the *m*, $\text{Me} > \text{Cl} > \text{Br}$; in the *p*, $\text{OMe} > \text{Me} > \text{Cl} > \text{Br}$, but the differences between the values for the halogen atoms is only slight.⁵⁴

2:6-Diethoxybenzonitrile cannot be caused, under any conditions, to pass into the corresponding ketone, $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{COR}$, by the action of a Grignard reagent, RMgX .⁵⁵

The effect of steric hindrance on (*a*) the rate of formation of the nitrates of substituted benzophenones, (*b*) the yield of Schiff's bases obtained by the condensation of substituted benzophenones with aniline and its homologues, and (*c*) the rate of hydrolysis of these Schiff's bases has been studied.⁵⁶ The last case is particularly interesting. Schiff's bases yield with alcoholic hydrogen chloride coloured additive compounds which gradually fade and become colourless as hydrolysis takes place. The times required for complete decolorisation were as follows:

Benzophenone-anil	30—35 seconds.
Benzophenone- <i>o</i> -tolil	4½—5 minutes.
Benzophenone- <i>m</i> -tolil	35—40 seconds.
Benzophenone- <i>p</i> -tolil	50—60 „
<i>p</i> -Tolylphenylketone-anil	50—60 „
<i>o</i> -Tolylphenylketone-anil	19—20 minutes.
Benzophenone-mesil	10½—11 hours.

The influence of ortho-substituents is well marked, as one would expect, but it is certainly remarkable that the ortho-methyl group of phenyl *o*-tolyl ketone should have so much greater influence than the ortho-methyl group of *o*-toluidine. This result is held to support Pfeiffer's theory of halochromy,⁵⁷ which requires that the addition of water to a C:N-linking on hydrolysis should take place at the carbon, and not at the nitrogen atom. Thus:



Condensation.

The condensation of γ -ketonic acids with aldehydes has been studied with interesting results. The simplest γ -ketonic acid, lævulic acid, presents the possibilities that condensation with benzaldehyde may take place (1) as with a derivative of acetone, yielding β - or δ -substituted benzylidenelævulic acids, or (2) as with a

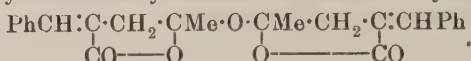
⁵⁴ O. C. M. Davis and F. W. Rixon, *T.*, 1915, **107**, 728; *A.*, ii, 537.

⁵⁵ E. E. Turner, *T.*, 1915, **107**, 1459.

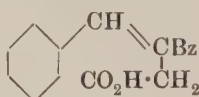
⁵⁶ G. Reddelien, *Ber.*, 1915, **48**, 1462; *A.*, 1916, i, 48.

⁵⁷ *Annalen*, 1910, **376**, 285; 1911, **383**, 92; *A.*, 1910, i, 852; 1911, i, 788.

derivative of acetic acid, forming the α -substituted acid. Earlier work has shown that condensation in alkaline solution leads to the δ -acid, whilst the β -acid is formed by heating the components with anhydrous sodium acetate.⁵⁸ It has now been shown that, when sodium lævulate is heated with benzaldehyde and acetic anhydride, that is, under the conditions used in Perkin's synthesis of cinnamic acid, a product is formed which has the probable constitution given below, for it yields α -benzylidenelævulic acid on hydrolysis.⁵⁹



β -Benzoylpropionic acid, $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, when condensed with benzaldehyde in the presence of alkali hydroxides or hydrogen chloride, behaves as a derivative of acetophenone, yielding β -benzoyl- β -benzylidenepropionic acid (I), which readily gives 3-benzoyl- α -naphthol (II) on heating.



(I.)

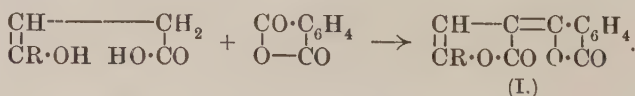


(II.)

When sodium β -benzoylpropionate is heated with benzaldehyde and acetic anhydride, however, two molecular proportions of water are eliminated, and γ -phenyl- α -benzylidenecrotonolactone is formed⁶⁰:



γ -Ketonic acids also suffer condensation at the α -position when their sodium salts are heated with phthalic anhydride and acetic anhydride,⁶¹ the products being double lactones of the type (I) shown below:



The condensation product of β -*p*-toluoylpropionic acid and phthalic anhydride, which has been most fully studied, is converted by sodium ethoxide into the sodium derivative of the diethyl ester (II) of the corresponding dicarboxylic acid. The diethyl ester is

⁵⁸ H. Erdmann, *Ber.*, 1885, **18**, 3441; *Annalen*, 1889, **254**, 182; 1890, **258**, 129; E. Erlenmeyer, jun., *Ber.*, 1890, **23**, 74; *A.*, 1886, i, 241; 1890, i, 375, 495, 1129.

⁵⁹ W. Borsche, *ibid.*, 1915, **48**, 842; *A.*, i, 691.

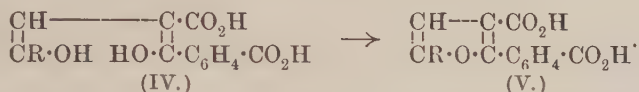
⁶⁰ W. Borsche, *ibid.*, 1914, **47**, 1108; *A.*, 1914, i, 686.

⁶¹ W. Borsche, *ibid.*, 2708; *A.*, i, 251.

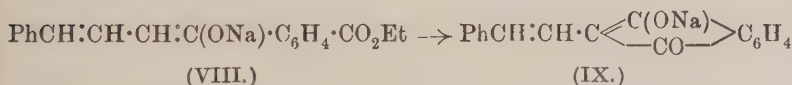
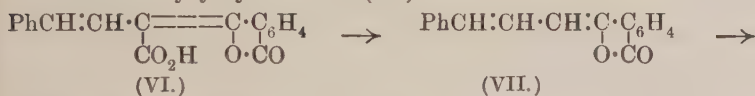
unstable, and when liberated from the sodium derivative passes into the lactone (III):



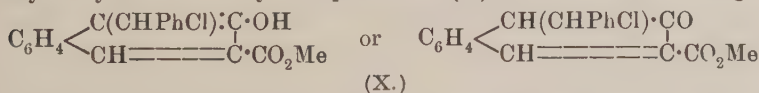
This substance, when heated, loses a molecular proportion of alcohol, and yields an isomeride of the original condensation product (I), which can only be a stereoisomeride, owing its separate existence to the ethylene linking in the molecule. Both isomerides pass smoothly into the furan derivative (V), possibly through the intermediate product (IV), when heated with alcoholic sulphuric acid:



γ -Phenylisocrotonic acid, itself, like its γ -hydroxyl derivative (the enolic form of β -benzoylpropionic acid) can be condensed with phthalic anhydride under the same conditions, yielding α -phthalylidene- γ -phenylisocrotonic acid (VI), which is readily converted into cinnamylidenephthalide (VII). This substance when treated with sodium alkoxide gives an unstable compound (VIII), which is analogous to the substance II, but immediately suffers the loss of a molecular proportion of alcohol, giving the sodium derivative of 1:3-diketo-2-styrylhydrindene (IX)⁶²:



The condensation of methyl 2-hydroxy-3-naphthoate with benzaldehyde in the presence of hydrogen chloride gives methyl 2-hydroxy-1-chlorobenzyl-3-naphthoate (X), in which the halogen



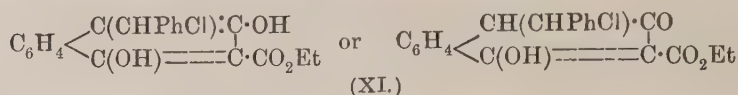
atoms are extremely reactive, being readily displaced by other groups, such as hydroxyl or anilino-groups.⁶³ When the same ester is condensed with terephthalaldehyde a similar product is obtained, only one of the aldehyde groups entering into the reaction.⁶⁴ Ethyl

⁶² W. Borsche and G. Heimburger, *Ber.*, 1915, **48**, 966; *A.*, i, 680.

⁶³ F. Friedl, *Monatsh.*, 1910, **31**, 917; *A.*, 1910, i, 741.

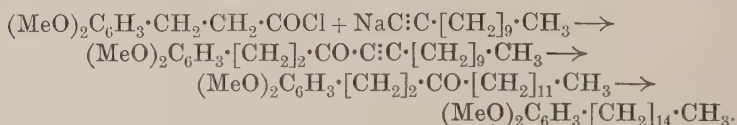
⁶⁴ K. Lugner, *ibid.*, 1915, **36**, 143; *A.*, i, 546.

1:3-dihydroxy-2-naphthoate similarly forms a condensation product (XI) with benzaldehyde and hydrogen chloride:



The halogen atom in this substance is even more reactive than that in the corresponding monohydroxy-derivative (X).⁶⁵

An unusual and important type of condensation has been employed in the synthesis of 1-*n*-pentadecyl-2:3-dimethoxybenzene (hydrourushiol dimethyl ether).⁶⁶ After many fruitless attempts to prepare this compound by the more obvious methods, the following procedure was adopted: 2:3-Dimethoxyphenylpropionyl chloride was condensed with sodium dodecinene, and the resulting unsaturated ketone was reduced first to the saturated ketone by hydrogen and platinum-black. Further reduction by Clemmensen's method⁷⁰ gave the required compound:



Dynamic Isomerism.

T. M. Lowry and V. Steele⁷¹ discuss the nomenclature of the phenomenon which is perhaps most generally termed tautomerism, and urge that the expression dynamic isomerism should be used for all cases in which isomerism passes from a static to a dynamic condition, whilst the words tautomeric and desmotropic should be used in the sense of the original definitions.

Tautomeric substances are, in this sense, compounds which may be represented by two alternative formulæ; they are not isomeric, but identical, as, for instance, 1:2- and 1:6-di-derivatives of benzene. The term desmotropy is reserved for those cases in which a definite grouping of atoms passes over into an isomeric grouping by a rearrangement of bonds consequent on the displacement of a hydrogen atom. Several interesting cases of dynamic isomerism have been investigated this year.

α - and α' -Chlorocamphors undergo mutarotation in the presence of alkali, so that each substance is converted into the same mixture

⁶⁵ H. Nowak, *Monatsh.*, 1914, **35**, 909; *A.*, i, 545.

⁶⁶ R. Majima and J. Tahara, *Ber.*, 1915, **48**, 1606; *A.*, 1916, i, 38.

⁷⁰ *Ann. Report*, 1914, 123.

⁷¹ *T.*, 1915, **107**, 1382; *A.*, i, 976.

of isomerides in equilibrium.⁷² On this fact is based a method of preparation of α' -chlorocamphor. α -Chlorocamphor is converted into the equilibrium mixture by means of alkali in alcoholic solution. The solution is acidified to prevent further isomeric change, and most of the α -chlorocamphor is then removed by crystallisation at -18° . The mother liquors then yield a crude α' -chlorocamphor, which is purified by fractional crystallisation. Pure α - and α' -chlorocamphors yield on nitration α -chloro- α' -nitrocamphor and α' -chloro- α -nitrocamphor respectively, but on bromination each chlorocamphor yields the same mixture of the two stereoisomeric chlorobromocamphors. It seems, therefore, that nitration of these ketones takes place by direct substitution, whilst bromination is the result of the addition of bromine to the common enolic form of α - and α' -chlorocamphors, and subsequent elimination of hydrogen bromide. The last result affords strong confirmation of Lapworth's theory⁷³ of the halogenation of ketones.

H. Leuchs⁷⁴ has shown that the optically active *o*-carboxy-2-benzyl-1-hydrindone yields with bromine a mixture of 90—95 per cent. of the inactive and 10—5 per cent. of the active brominated ketonic acid:



It was to be expected that the addition of bromine to the enolic form of the ketonic acid would yield an optically inactive product, and this author ascribes the formation of the active acid to direct substitution.

Both A. Lapworth⁷⁵ and K. H. Meyer⁷⁶ point out that its formation may be due to asymmetric synthesis caused by the addition of bromine to the enolised form of the acid in the presence of the unchanged optically active keto-form, a view which had been previously considered and rejected by Leuchs. Meyer compares the asymmetric synthesis with that of benzaldehydecyanohydrin,⁷⁷ but Leuchs⁷⁸ denies the analogy, and points out that it is difficult to see why methane, into which substituents such as halogen may be introduced, should become incapable of substitution when united to a ketonic carbonyl group. Incidentally, it may be noted that chlorination of the ketonic acid has given a similar result to that mentioned above.⁷⁹

Formyldeoxybenzoin occurs in two enolic forms, which might be

⁷² T. M. Lowry and V. Steele, *loc. cit.*, compare F. S. Kipping, *P.*, 1905, 21, 125.

⁷³ *T.*, 1904, 85, 30.

⁷⁴ *Ann. Report*, 1913, 62, 102.

⁷⁵ *P.*, 1913, 29, 289.

⁷⁶ *Ber.*, 1914, 47, 826; *A.*, 1914, ii, 351

⁷⁷ *Ann. Report*, 1912, 177.

⁷⁸ *Ber.*, 1914, 47, 2528; *A.*, i, 411.

⁷⁹ *ibid.*, 1915, 48, 1015; *A.*, i, 694.

either structural isomerides having the formulæ $\text{PhCO}\cdot\text{CPh}\cdot\text{CH}\cdot\text{OH}$ and $\text{PhC}(\text{OH})\cdot\text{CPh}\cdot\text{CHO}$, or stereoisomerides, both having one of these two structural formulæ. The former view was held previously,⁸⁰ the first formula being assigned to the yellow variety from analogy to benzil, and the second to the colourless variety, which was the more reactive towards Schiff's reagent, this indicating the presence of the aldehyde group. It is now shown that both varieties are oxidised by ozone to benzil and formic acid, and consequently have the first formula. They are, therefore, stereoisomerides.⁸¹

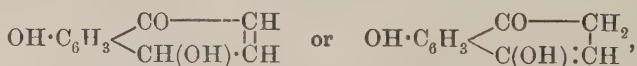
Acetylacetone forms condensation products with ammonia, primary amines and diethylamine, with loss of water, but not with methylaniline or benzylmethylamine; methylacetylacetone,



combines with ammonia and primary amines, but not with diethylamine; dimethylacetylacetone, $\text{MeCO}\cdot\text{CMe}_2\cdot\text{COMe}$, does not suffer condensation with ammonia. These facts suggest that the condensation is preceded by the addition of the amine to the enolic form of the ketone, and not to the carbonyl group⁸²:



A case of keto-enol isomerism in a phenol of the naphthalene group has been recorded.⁸³ Juglone (8-hydroxy-1:4-naphthoquinone) gives on reduction two isomeric hydrojuglones, which are readily interconvertible. Both yield the same triacetate, but only one variety reacts as a ketone, forming a semicarbazone and an oxime. The latter, therefore, has one of the two formulæ:



whilst its isomeride is 1:4:8-trihydroxynaphthalene.

Evidence has been brought forward in support of the view that phenylpyruvic acid exists in two desmotropic forms, the free acid being in the enolic form, and the normal salts in the ketonic form. The existence of the enolic form, first suggested by S. Ruhemann and H. E. Stapleton,⁸⁴ has been indicated by the preparation of an acetate having the constitution $\text{CHPh}\cdot\text{C}(\text{OAc})\cdot\text{CO}_2\text{H}$.⁸⁵ Phenylpyruvic acid and benzaldehyde condense with aqueous sodium

⁸⁰ W. Wislicenus and A. Rutting, *Annalen*, 1911, **379**, 229; *A.*, 1911, i, 303.

⁸¹ J. Scheiber and G. Hopfer, *Ber.*, 1914, **47**, 2704; *A.*, i, 267.

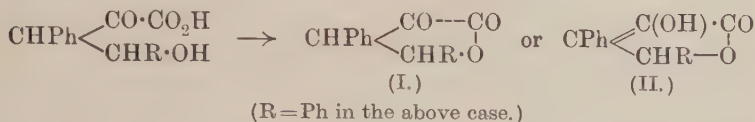
⁸² L. Rügheimer, *ibid.*, 2759; *A.*, i, 224.

⁸³ R. Willstätter and A. S. Wheeler, *ibid.*, 2796; *A.*, i, 268.

⁸⁴ *T.*, 1900, **77**, 239.

⁸⁵ J. Bougault and Mlle. R. Hemmerlé, *Compt. rend.*, 1915, **160**, 100; *A.*, i, 78.

hydroxide to give γ -hydroxy- α -keto- $\beta\gamma$ -diphenylbutyric acid. This suffers the loss of a molecular proportion of water when warmed with hydrochloric acid, giving a substance for which two formulæ are possible:



The same end-product results from the condensation of phenylpyruvic acid and benzaldehyde with hydrochloric acid, and many similar products have been obtained with other aromatic aldehydes. When piperonaldehyde or cuminaldehyde was used, a mixture of two isomeric lactones was formed. Each of these gave a distinct acetyl derivative, and the view was put forward that they were stereoisomerides, having, therefore, the ketonic formula I, of which two stereoisomeric modifications are possible, rather than the enolic formula II, which does not admit the existence of such isomerides. The acetyl derivatives were represented as *C*-substituted



A similar condensation product obtained by the action of formaldehyde and hydrochloric acid on α -oximino- β -phenylpropionic acid, and evidently formed by the condensation of formaldehyde with pyruvic acid, has now been examined. It gives an intense coloration with ferric chloride, and is found by titration by K. H. Meyer's method to consist almost entirely of the enolic form. It has no ketonic properties, nor have its acyl derivatives, which behave like *O*-acyl derivatives. Its properties thus show that it has the formula II (R=H).⁸⁷

The conclusions of Erlenmeyer and Lapworth as to the constitution of these lactones are thus opposed but each of them is apparently warranted. It is clear that further investigation of the subject is required.

Stereoisomerism.

Racemisation of Acids.—The literature dealing with the racemisation of acids has been reviewed and discussed by A. McKenzie and Miss S. T. Widdows.⁸⁸ Optically active acids having the asymmetric carbon atom in the α -position are readily racemised by means of alkali only when at least one of the groups attached to

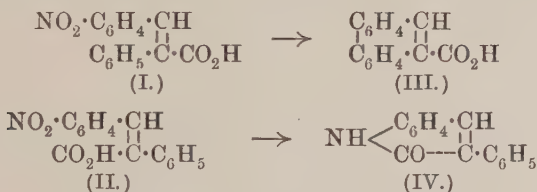
⁸⁶ E. Erlenmeyer, *jun.*, *Ber.*, 1905, **38**, 3119; *A.*, 1905, **i**, 783. See also references given in the next paper.

⁸⁷ N. Hall, J. E. Hynes and A. Lapworth, *T.*, 1915, **107**, 132.

⁸⁸ *T.*, 1915, **107**, 702; *A.*, **i**, 814.

Another interesting resolution is that of the phenylglyceric acid derived from cinnamic acid by oxidation. The stereoisomeric inactive phenylglyceric acid derived from *allocinnamic* acid was resolved many years ago,⁹² but its isomeride could not be resolved at that time, and there was some discussion as to the reason for its non-resolution. It has now been shown that the acid in question may be resolved by crystallisation of its morphine salt from absolute acetone.⁹³

Cinnamic Acids and Stilbenes.—The configuration of the stereoisomeric stilbenes has been determined by a method similar to that employed for the cinnamic acids.⁹⁴ The stable 2-nitro- α -phenylcinnamic acid and the labile *allo*-acid behave differently in chemical reactions. The former when reduced and diazotised yields phenanthrene-9-carboxylic acid (III) readily, whilst the latter fails to give a trace of this substance. Moreover, the amino-acid obtained by reducing the *allo*-nitro-acid can only exist in the form of salts or of the lactam, 3-phenylcarbostyryl (IV). The stable acid has, therefore, the *cis*-configuration (I), and the labile acid the *trans*-configuration (II), the terms *cis* and *trans* referring here to the relative positions of the phenyl groups:



When *trans*-2-nitro- α -phenylcinnamic acid is reduced and the amino-group replaced by hydrogen, *allo*- α -phenylcinnamic acid is obtained. This has, therefore, the *trans*-configuration, and it follows that the stable α -phenylcinnamic acid has the *cis*-configuration. These acids lose carbon dioxide when heated at 300° with barium oxide under diminished pressure, and the *cis*-acid yields *isostilbene* with a little stilbene, whilst the *trans*-acid yields much stilbene with some *isostilbene*. *isoStilbene* has therefore the *cis*-, and stilbene the *trans*-configuration.⁹⁵ The two known modifications of α -methylcinnamic acid (m. p. 81—82° and 73—74°) prove to be dimorphous forms of the same acid. Both form the same methyl ester, and cannot be converted into methylindone. Either can be converted by

⁹² J. Plöchl and B. Mayer, *Ber.*, 1897, **30**, 1600; *A.*, 1897, i, 528.

⁹³ C. N. Riiber, *ibid.*, 1915, **48**, 823; *A.*, i, 544.

⁹⁴ R. Stoermer and P. Heymann, *ibid.*, 1912, **45**, 3099; *A.*, 1912, i, 974.

⁹⁵ R. Stoermer, *Annalen*, 1915, **409**, 13; with L. Prigge, *ibid.*, 20; *A.*, i, 682, 683.

the light of a quartz lamp into *allo-α*-methylcinnamic acid (m. p. 91—92°), a new modification which forms a distinct methyl ester. This acid is easily converted into 2-methylindone, and hence contains the phenyl and carboxyl groups in the *cis*-positions to each other⁹⁶:



The stereoisomeric stilbene dibromides behave differently with pyridine, the *α*-form losing bromine with regeneration of stilbene, whilst the *β*-form of lower melting point loses hydrogen bromide in the normal manner, yielding bromostilbene (m. p. 31°). This difference in chemical behaviour of stereoisomerides is also shown to some extent by the dibromocinnamic acids, but here the *α*-form only suffers the loss of bromine as such to the extent of 62 per cent., the remainder losing hydrogen bromide to give *α*-bromocinnamic acid. *β*-Dibromocinnamic acid gives a quantitative yield of *α*-bromocinnamic acid. In the case of aliphatic compounds of similar constitution, dibromocrotonic acid and dibromosuccinic acid, both forms lose hydrogen bromide when treated with pyridine.⁹⁷

In this connexion, some experiments on the elimination of bromine from dibromoanisylideneacetophenone,



are of interest. This compound readily exchanges one bromine atom for alkyloxy when boiled with methyl or ethyl alcohols. When boiled with propyl, *isobutyl*, or benzyl alcohols, or glacial acetic acid, it is converted into monobromoanisylideneacetophenone, and when boiled with *isopropyl* or *tert.*-butyl alcohols, acetone or benzoin, into anisylideneacetophenone.⁹⁸

Asymmetric Synthesis.—E. Erlenmeyer, jun.,⁹⁹ has shown that when benzaldehyde is heated with *d*-tartaric acid in alcoholic solution, the original rotatory power of the solution is increased, and that the solution, after thorough washing to remove tartaric acid, remains slightly *lævorotatory*. From this '*l*-benzaldehyde' a mandelonitrile having slight *l*-power, and a mandelic acid having slight *d*-power, were prepared in a chemically, but not optically pure state. It now appears¹ that this '*l*-benzaldehyde' owes its optical activity to certain non-volatile impurities, namely, benzyl-

⁹⁶ R. Stoermer and G. Voht, *Annalen*, 1915, **409**, 36; *A.*, i, 684.

⁹⁷ P. Pfeiffer, *Ber.*, 1912, **45**, 1819; with K. von Swidzinski, *ibid.*, 1915, **48**, 1048; *A.*, 1912, i, 618; 1915, i, 793.

⁹⁸ F. J. Wilson and A. A. Boon, *Pharm. J.*, 1915, **94**, 486; *A.*, i, 413.

⁹⁹ *Ann. Report*, 1914, 68.

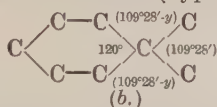
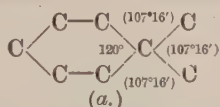
¹ E. Erlenmeyer, jun., *Biochem. Zeitsch.*, 1914, **66**, 509; *A.*, i, 257; with G. Hilgendorff, *ibid.*, 1914, **68**, 351; *A.*, i, 408; E. Wedekind, *Ber.*, 1914, **47**, 3172; *A.*, i, 256.

idenedioxysuccinic acid, $\text{CHPh} \begin{smallmatrix} \text{O} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \text{O} \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, and its ethyl ester, and there is no longer any definite evidence that benzaldehyde may be regarded as a substance with 'induced' asymmetry having the formula $\text{CPh} \begin{smallmatrix} \text{H} \\ \text{OL} \\ \text{L} \end{smallmatrix}$, where L represents an unoccupied position, or an electron.²

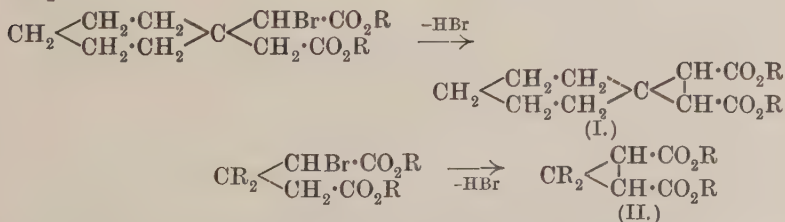
The formation of optically active mandelonitrile and mandelic acid is held by Erlenmeyer to demonstrate the temporary existence of 'l-benzaldehyde,' but it appears more probable that these substances result from asymmetric synthesis.

Spiro-compounds.

An interesting study has been carried out with the aid of *spiro*-compounds.³ In accordance with Baeyer's strain hypothesis, the normal angle of the tetrahedron ($109^\circ 28'$) has to be altered to an angle of 120° to produce the *cyclohexane* ring. The question arises whether the two side-chains attached to a carbon atom of this ring take up a symmetrical position with respect to each other and the two valencies participating in the ring, in which case the angle between them is found by calculation to be $107^\circ 16'$ (hypothesis *a*), or whether their direction is independent of those of the two valencies participating in the ring, so that they still remain inclined to one another at the tetrahedral angle of $109^\circ 28'$ (hypothesis *b*).



If hypothesis *a* is correct, there should be a greater tendency to form the *spiro*-compound I than there is to form the ring-compound II, owing to the closer proximity of the groups attached to the carbon atoms of the side-chains in the former case, and, moreover, the ring-compound I should be more stable than the ring-compound II:



² H. Pauly, *Biochem. Zeitsch.*, 1914, **67**, 439; *A.*, i, 257.

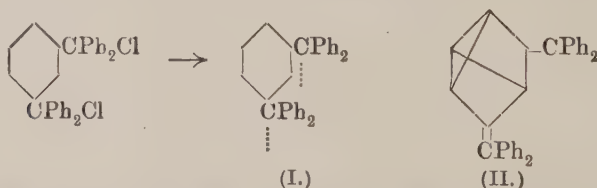
³ R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *T.*, 1915, **107**, 1080; *A.*, i, 816.

whereas if hypothesis *b* is correct, then the tendency should be the same in both cases. The results of experiments on the formation and stability of ring compounds of the two types point clearly to the correctness of hypothesis *a*.

Organic Radicles.

Since the discovery of triphenylmethyl, a large amount of work has been carried out on allied substances of the general formula R_3C , and this has been reviewed in previous Reports from time to time. This year there are again several interesting papers on this subject, and, moreover, different workers have recently been investigating the dissociation of peroxides, hydrazines, and disulphides into free radicles; a brief account of this development of the work is given below.

Metaquinonoid or Triarylmethyl.—The removal of the halogen atoms from tetraphenyl-*m*-xylylene dichloride by means of metals gives rise to a hydrocarbon, for which two different formulæ have been advocated.



O. Stark and O. Garben,⁴ finding that the properties of the substance were similar to those of Thiele's tetraphenyl-*p*-xylylene, and especially that it was indifferent to oxygen, proposed the metaquinonoid formula (II). W. Schlenk and M. Brauns⁵ cannot confirm Stark and Garben's results, and find that the product is very easily oxidisable. They now show that it is a bistriarylmethyl having the formula (I). The reaction proceeds in two stages. One of the halogen atoms is easily removed, giving a substance having the properties both of a triarylmethyl and of a triarylmethyl chloride, whilst the second halogen atom can be removed by more vigorous treatment, giving a bistriarylmethyl. The fact that tetraphenyl-*m*-xylylene dichloride yields a bistriarylmethyl, whereas the isomeric para-dichloride yields a quinonoid substance, is an indication that metaquinonoid substances do not exist.

The intention to prepare the corresponding ortho-compound⁶ was not realised, for the required tetraphenyl-*o*-xylylene dichloride

⁴ *Ann. Report*, 1913, 107.

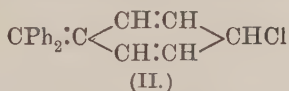
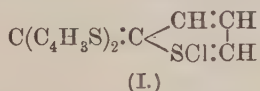
⁵ *Ber.*, 1915, 48, 661; *A.*, i, 517.

⁶ W. Schlenk and M. Brauns, *ibid.*, 716; *A.*, i, 518.

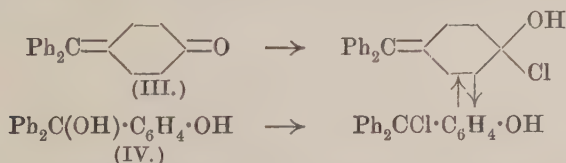
could not be obtained, the action of all chlorinating agents on the corresponding glycol forming the anhydride.



The question whether the coloured triarylcannabinol salts are to be regarded as carbonium compounds or quinonoid derivatives ("quinocarbonium" salts) is still under discussion. Two independent investigations have been carried out with the view of preparing tri- α -thienylcannabinol, $\text{HO} \cdot \text{C} : \left(\cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{CH} \\ \text{S} \text{---} \text{CH} \end{array} \right)_3$, in order to compare it with triarylcannabinols. Neither resulted in the isolation of the pure cannabinol, owing to its instability; but W. Schlenk and R. Ochs⁷ prepared the perchlorate in a pure state, and find that it closely resembles triphenylmethyl perchlorate in physical properties. They hold that the former cannot be represented in the quinonoid form, and that it is therefore unnecessary to assume such form for salts of the latter type, for which the carbonium-salt formula, $\text{R}_3\text{C-X}$, is adequate. A. E. Tschitschibabin and N. N. Gavrilov,⁸ who prepared a double chloride of trithienylcannabinol and zinc, $2(\text{C}_4\text{H}_3\text{S})_3\text{CCl}_2 \cdot \text{ZnCl}_2$, offer the alternative explanations that the chloride has either the carbonium-salt formula or a formula I analogous to the "quinocarbonium" formula II.



Attempts to prepare *p*-hydroxytriphenylmethyl have been unsuccessful. Both fuchsone (III) and *p*-hydroxytriphenylcannabinol (IV) yield *p*-hydroxytriphenylcannabinyl chloride on exposure to hydrogen chloride, hence the usual equilibrium between the two isomeric forms of the chloride must be assumed. When this sub-



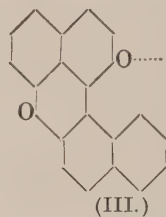
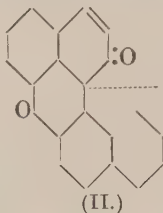
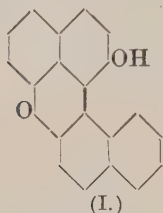
stance is treated with molecular silver, a molecule of hydrogen chloride is removed instead of the usual single chlorine atom, giving, consequently, fuchsone instead of *p*-hydroxytriphenylmethyl. *p*-Carboethoxy-, *p*-benzoxy-, and *p*-acetoxy-triphenylcarb-

⁷ *Ber.*, 1915, **48**, 676; *A.*, i, 579.

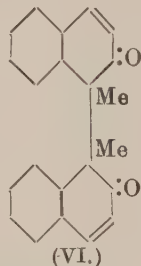
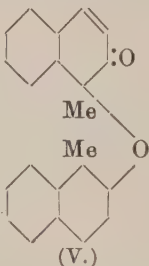
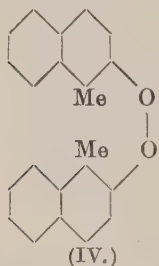
⁸ *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1614; *A.*, i, 578.

inyl chlorides, however, yield the respective free radicles, but these are too unstable to be isolated as such.⁹

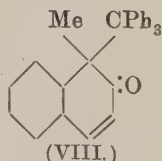
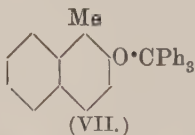
α-Ketomethyl or Aroxyl Radicles.—Space forbids more than a passing reference to the organic radicle derived from hydroxydinaphthalene oxide (I). It possesses a tervalent carbon atom and has the “α-ketomethyl” formula (II), but can also react in the isomeric “aroxyl” form (III) with a univalent oxygen atom.¹⁰



Methyl-β-naphthol can be oxidised to dehydro-1-methyl-β-naphthol, for which there are three possible formulæ.



The peroxide formula (IV) is supported by the oxidising properties of the substance; the other two formulæ (V and VI) by the sensitiveness to permanganate in indifferent solvents. The compound combines with triphenylmethyl to form triphenylmethyl 1-methyl-β-naphthyl ether, which has the formula (VII), not (VIII), since it is not sensitive to permanganate.



It is possible that the formation of this substance is due to the dissociation of dehydro-1-methyl-β-naphthol into an aroxyl radicle,

⁹ M. Gomberg and R. L. Jickling, *J. Amer. Chem. Soc.*, 1915, **37**, 2575; *A.*, 1916, i, 29.

¹⁰ R. Punmerer and F. Frankfurter, *Ber.*, 1914, **47**, 1472; *A.*, 1914, i, 714.

but the existence of this cannot be proved by molecular-weight determinations or optical methods.¹¹

Hydrazines.—The study of the dissociation of tetra-arylhydrazines into free radicles has been continued by H. Wieland.¹² The introduction of nitro- or phenyl groups into the aryl nuclei hinders the dissociation, whilst the introduction of methyl, methoxyl, or dimethylamino-groups favours it in increasing degree. Tetra-*p*-dimethylaminotetraphenylhydrazine,

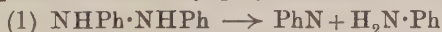


is colourless in the solid condition, but gives intense yellow solutions in indifferent solvents. Molecular-weight determinations show that it dissociates to the extent of 10 per cent. in benzene and 21 per cent. in nitrobenzene. Its decomposition in solution is very largely due to the dissociated fragment bis(dimethylaminophenyl)nitrogen, $(\text{NMe}_2 \cdot \text{C}_6\text{H}_4)_2\text{N}$, for the decomposition takes place twice as quickly in nitrobenzene as in benzene solution.

Triphenylhydrazine¹³ represents an interesting case, for there are two possible ways in which it may dissociate, namely, (1) $\text{Ph}_2\text{N} \cdot \text{NHPh} \rightarrow \text{Ph}_2\text{N} + \text{NHPh}$ and (2) $\text{Ph}_2\text{N} \cdot \text{NHPh} \rightarrow \text{Ph}_2\text{NH} + \text{NPh}$.

Study of its decomposition in boiling xylene solution indicates that the second expression represents the course of the reaction, for the products found are diphenylamine, azobenzene (presumably produced by polymerisation of NPh), and quinoneanildiphenylhydrazone, $\text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{NPh}_2$. This substance may well be formed by the addition of the phenylnitrogen (PhN) radicle to an intact molecule of triphenylhydrazine, and subsequent loss of hydrogen from the product.

J. Stieglitz and G. O. Curme¹⁴ have shown that the spontaneous decomposition of hydrazobenzene into azobenzene and aniline behaves as a unimolecular reaction, and represent the course of the reaction as a dissociation of hydrazobenzene into aniline and a free radicle, PhN, with univalent nitrogen, proceeding at a measurable speed, followed by polymerisation of the PhN radicle



to azobenzene with immeasurably great velocity. H. Wieland¹⁵ observes that dissociation of a hydrazine containing only two phenyl substituents is contrary to experience, and holds that the

¹¹ R. Pummerer and E. Cherbuliez, *Ber.*, 1914, **47**, 2957; *A.*, i, 417.

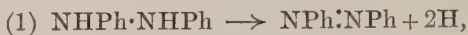
¹² H. Wieland, *ibid.*, 1915, **48**, 1078; *A.*, i, 848.

¹³ H. Wieland and A. Reverdy, *ibid.*, 1112; *A.*, i, 851.

¹⁴ *Ibid.*, 1913, **46**, 911; *A.*, 1913, ii, 398.

¹⁵ *Ibid.*, 1915, **48**, 1098; *A.*, i, 850.

decomposition of hydrazobenzene takes place in two stages, as follows:

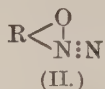
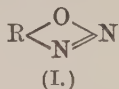


of which the first proceeds at a measurable speed, whilst the second takes place with immeasurably great velocity. In order to discriminate between the two views, he has studied the spontaneous decompositions of asymmetric hydrazo-compounds of the type $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{X}$. If the view of Stieglitz and Curme is correct, a mixture of the three azo-compounds $\text{NPh} : \text{NPh}$, $\text{NPh} : \text{N} \cdot \text{C}_6\text{H}_4\text{X}$, and $\text{XC}_6\text{H}_4 : \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{X}$ should result, but Wieland finds that the homogeneous asymmetric azo-compound, $\text{NPh} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{X}$, is alone produced, as required by his own hypothesis.

Disulphides.—The properties of diphenyl disulphide have been compared with those of hexa-arylethanes. The change of colour of the former in benzene and xylene obeys Beer's colorimetric dilution law, so that a dissociation equilibrium, $\text{PhS} \cdot \text{SPh} \rightleftharpoons 2\text{PhS}$, is not supported.¹⁶

Diazo-compounds.

Diazophenols.—The constitution of the internal diazo-oxides, or so-called diazophenols, has again received attention. Last year Klemenc,¹⁷ discussing the three possible formulæ, pointed out that Wolff's work had rendered the cyclic diazo-oxide structure (I) improbable, and supported the diazonium formula (II) as against



the quinonediazide formula (III) on the grounds that, (i) diazophenols dissolve in concentrated acids without decomposition, (ii) they are only sparingly soluble in organic solvents, and (iii) they are formed in acid solution. G. T. Morgan and J. W. Porter¹⁸ now reject formula (II), and conclude that (I) is more generally serviceable than (III), although the last two are not irreconcilable. Klemenc's argument (i) is not answered, but it is shown that sparing solubility in organic media and formation in acid solution are not general properties of internal diazo-oxides. The yellow colour of these internal diazo-oxides, and the non-existence of internal metadiazido-oxides,¹⁹ furnish strong arguments

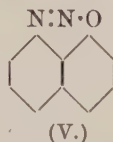
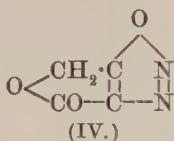
¹⁶ H. Lecher, *Ber.*, 1915, **48**, 524; *A.*, i, 532.

¹⁷ *Ann. Report*, 1914, 102.

¹⁸ *T.*, 1915, **107**, 645; *A.*, i, 599.

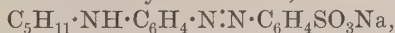
¹⁹ See also E. Bamberger, *Ber.*, 1915, **48**, 1354; *A.*, i, 1055.

in favour of the quinonediazide formula (III). The latter formula is also supported by the marked contrast between the reactivity of the internal diazo-oxides and the inertness of ortho-diazoimines and ortho-diazosulphides. On the other hand, it is urged in favour of the cyclic diazo-oxide formula (I) that (a) the colour of the substances in question is not incompatible with the presence in their molecules of the group $\cdot\text{N}:\text{N}\cdot\text{O}\cdot$, for this group is also present in the coloured diazo-oxides, $\text{R}\cdot\text{N}:\text{N}\cdot\text{O}\cdot\text{R}$; (b) the diazo-complex in internal diazo-oxides may have the same structure as in Wolff's diazotetronic anhydride (IV) in spite of the differences in their properties, for these may be ascribed to the absence of an



aromatic nucleus in the latter compound; (c) the existence of *peridiazo-oxides*, such as (V), renders the quinonediazide configuration generally inapplicable.

Coupling.—K. H. Meyer²⁰ holds the view that the coupling of diazonium salts with phenols or phenolic ethers is due to the addition of the diazo-salt to a double bond or to the conjugated double bond of the second component, whilst K. von Auwers and F. Michaelis²¹ suppose that the first stage is the addition of the diazo-salt to the oxygen atom of the hydroxyl or alkyloxyl group by reason of its residual affinity. P. Karrer²² now brings forward certain evidence to show that the addition of diazo-salts to amines takes place at the nitrogen atom. When *diisoamylaniline* is coupled with sodium diazobenzene-*p*-sulphonate, an alkyl group is eliminated, and the monoalkyl derivative,



is obtained; whereas dialkylanilines with small alkyl groups, such as dimethylaniline, give the normal dialkylaminoazobenzene-sulphonates. Now, the heavy *isoamyl* groups absorb more of the residual affinity of the nitrogen atom than the methyl groups; consequently, in the former compounds certain affinities, marked in the formula given below, are strengthened as com-



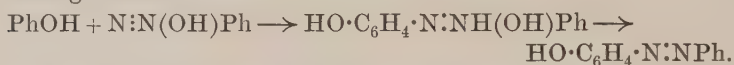
pared with those in dimethylaniline. Accordingly, if Meyer's

²⁰ *Ann. Report*, 1914, 100.

²¹ *Ber.*, 1914, **47**, 1275; *A.*, 1914, i, 744.

²² *Ibid.*, 1915, **48**, 1398; *A.*, i, 1073.

view were correct, diisoamylaniline should couple more readily than dimethylaniline, but this is not the case. It does not couple at all until one of the alkyl groups has been eliminated. If, however, the addition takes place at the nitrogen atom, the facts are readily explained; the diisoamyl groups absorb so much of the affinity of the nitrogen atom that addition of the diazonium salt is impossible until one of the alkyl groups has been eliminated. These and other considerations, such as the steric hindrance to coupling observed with ortho-substituted amines or phenols, and the existence of intermediate products of the type $\text{PhO}\cdot\text{N}:\text{N}\cdot\text{R}$, present a strong case for the view that coupling takes place by the addition of the diazonium salt to the oxygen or nitrogen atom of phenols and amines, forming intermediate oxonium or ammonium compounds, which subsequently undergo intramolecular change. The mechanism of coupling has also been discussed by G. Charrier,²³ who suggests that it takes place according to the following scheme:



Diazonium Perhaloids.—F. D. Chattaway²⁴ records the fact that ammonium perhaloids, of which he has prepared two new examples, $\text{NH}_4\text{Cl}_2\text{I}$ and NH_4ClBrI , are readily soluble in water and lose two-thirds of their halogen when exposed to a vacuum over lime. The diazonium perhaloids, on the other hand, are sparingly soluble in water and stable when kept in a vacuum over lime. Contrasting these properties of the two classes of substances, he finds support for his view²⁵ that diazonium trihaloids are not perhaloids at all, but *N*-trihalogenohydrazines, $\text{R}\cdot\text{NX}\cdot\text{NX}_2$. M. O. Forster²⁶ criticises Chattaway's conclusion, and A. Hantzsch²⁷ brings forward evidence against it. The latter author points out that benzenediazonium perbromide, $\text{N}:\text{NPhBr}_3$, should be compared rather with phenyltrimethylammonium perbromide, $\text{PhMe}_3\text{N}\cdot\text{Br}_3$, than with ammonium perbromides containing unsubstituted hydrogen atoms on the nitrogen atom. Phenyltrimethylammonium perbromide, however, is sparingly soluble in water and stable when exposed to a vacuum over lime, just like benzenediazonium perbromide. The former can only have the formula $\text{PhMe}_3\text{NBr}_3$, and there is consequently no necessity to assume for benzenediazonium perbromide any formula other than $\text{N}:\text{NPhBr}_3$ to explain the nature of its solubility and stability.

Forster discusses the formation of phenylazoimide by the action

²³ *Gazzetta*, 1914, **44**, ii, 503; *A.*, i, 66.

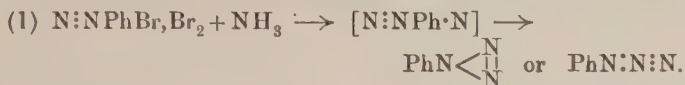
²⁴ *T.*, 1915, **107**, 105.

²⁵ *Ann. Report*, 1909, 97.

²⁶ *T.*, 1915, **107**, 260; *A.*, i, 181.

²⁷ *Ber.*, 1915, **48**, 1344; *A.*, i, 1073.

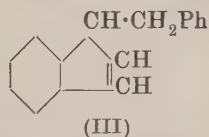
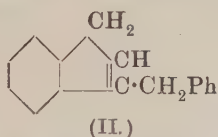
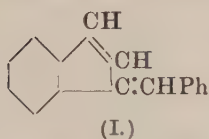
of ammonia on benzenediazonium perbromide, and points out that if the diazonium perbromides are to be regarded as *N*-tribromohydrazines, as Chattaway claims, there appears to be no alternative to the cyclic structure, $\text{Ph}\cdot\text{N}<\begin{smallmatrix}\text{N}\\\text{N}\end{smallmatrix}$, for phenylazoimide. The diazonium perhaloid representation, however, permits the explanation of the formation of phenylazoimide in two ways, as follows:



The second explanation depends on the production and momentary existence of bromoamine giving rise to a diazobromoamine which loses hydrogen bromide, owing to the excess of ammonia present. Evidence of the possibility of this explanation is afforded by the fact that the action of chloroamine on a diazonium salt yields a certain amount of the azoimide.

Polycyclic Aromatic Hydrocarbons.

Indene.—The methylene group in indene is capable of condensation and alkylation. With benzaldehyde, benzylideneindene (phenylbenzofulvene) (I) is formed, and this on reduction yields 3-benzylidene (II), of which the constitution follows from the fact that it can be condensed with benzaldehyde, forming benzylidenebenzylindene, and therefore contains a methylene group. When indene is alkylated by means of benzyl chloride and alkali it also yields 3-benzylindene in the place of the expected 1-benzyl-



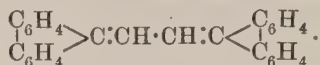
indene (III). To explain this and similar phenomena, Thiele²⁸ put forward the theory of the oscillation of the double linking in the indene nucleus. C. Courtot,²⁹ however, has now shown that in this case and others both the 1- and 3-substituted indenenes can be isolated, and there is therefore no necessity for Thiele's theory. It is the alkali used in the condensation of benzyl chloride with indene that is responsible for the change to the isomeric form. Thus, 1-benzylindene can be prepared by the action of benzyl

²⁸ *Ann. Report*, 1906, 134.

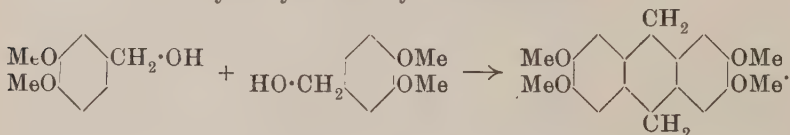
²⁹ *Compt. rend.*, 1915, 160, 523; *A.*, i, 392.

chloride on magnesium indene bromide, but alcoholic potassium hydroxide converts it into 3-benzylindene. The 1- and 3-benzylindenes differ in physical and also in chemical properties, the latter combining with bromine to form an unstable compound which almost immediately loses hydrogen bromide, leaving benzylideneindene, whilst the former gives a liquid dibromide which does not spontaneously lose hydrogen bromide, and when treated with pyridine only yields resinous products.

Fluorene.—Dinaphthafluorene is obtained in a 60 per cent. yield by the action of glacial phosphoric acid on di- α -naphthylcarbinol for one hour at 175°. ³⁰ Attention may also be drawn to the discovery ³¹ that the red hydrocarbon, often formed as a by-product when condensations with fluorene are carried out in the presence of sodium ethoxide, is $\alpha\delta$ -bisdiphenylene- $\Delta^{\alpha\gamma}$ -butadiene,



Anthracene.—The constitution of the compounds obtained by the action of mineral acids on homopiperonyl and homoveratryl alcohols has now been established. These substances are derivatives of 2:3:6:7-tetrahydroxy-9:10-dihydroanthracene.



Tetramethoxydihydroanthracene is, however, best prepared by the condensation of veratrole with formaldehyde by means of 60 per cent. sulphuric acid, when it is obtained in a quantitative yield. The dihydroanthracene ring suffers disruption when this compound is nitrated, 6:6'-dinitro-3:4:3':4'-tetramethoxydiphenylmethane being formed. ³²

A method for the preparation of 9:10-diphenylanthracene is as follows. *o*-Phthalaldehydic acid treated with magnesium phenyl bromide in boiling anisole yields *o*- α -benzhydrylbenzhydrol,



which on boiling with hydrobromic acid gives 9:10-diphenylanthracene. This substance does not yield anthraquinone, but *o*-dibenzoylbenzene, on oxidation with chromic acid. ³³

The oxidation of quinizarin (1:4-dihydroxyanthraquinone) in

³⁰ A. E. Tschitschibabin and O. J. Magidson, *J. pr. Chem.*, 1914, [ii], **90**, 168; *A.*, i, 239

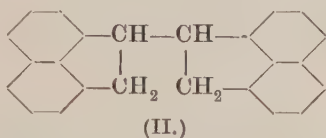
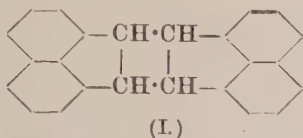
³¹ W. Wislicenus, *Ber.*, 1915, **48**, 617; *A.*, i, 519.

³² Mrs. G. M. Robinson, *T.*, 1915, **107**, 267; *A.*, i, 233.

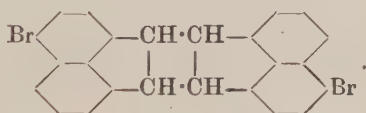
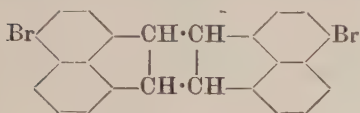
³³ H. Simonis and P. Remmert, *Ber.*, 1915, **48**, 406; *A.*, i, 136.

hot benzene solution with lead dioxide leads to 1:4:9:10-anthradiquinone, which has typical quinonoid properties. Attempts to prepare 1:2:9:10-anthradiquinone and 1:4:5:8:9:10-anthratriquinone from alizarin and 1:4:5:8-tetrahydroxyanthraquinone respectively were unsuccessful.³⁴

Acenaphthylene.—Acenaphthylene polymerises under the influence of light, giving a mixture of the two *cis-trans* isomeric heptacyclenes (I), both of which on reduction yield diacenaphthyl (II).

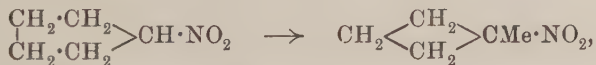


Each heptacyclic compound yields two dibromo-derivatives, all of which undergo oxidation quantitatively to α -bromonaphthalic anhydride, this fact indicating the formulæ given below for the two dibromides of each hydrocarbon.³⁵



Hydrocyclic Compounds and Terpenes.

Isomerisation of ring compounds usually proceeds in such a manner that cyclic compounds containing a side-chain are transformed into larger rings, whilst those without side-chains give smaller rings with side-chains. Thus, *cyclopentyl* nitrite, prepared by the action of silver nitrite on *cyclopentyl* iodide, yields 1-nitro-1-methyl*cyclobutane*, amongst other products of the reaction, when treated with concentrated alkali hydroxide solution,



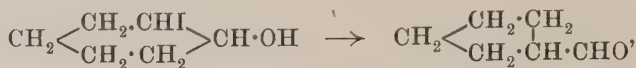
whilst iodomethyl*cyclopentane* yields with silver nitrite principally 1-nitro-1-methyl*cyclopentane* with some ω -nitromethyl*cyclopentane* and traces of nitro*cyclohexane*. The isomerisation of a five- to a six-membered ring is also illustrated by the formation of *cyclohexene* from *cyclopentylcarbinol* by the action of oxalic acid.³⁶

³⁴ R. Lesser, *Ber.*, 1914, **47**, 2526; *A.*, i, 420.

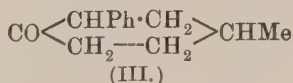
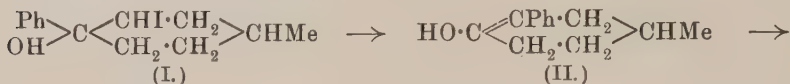
³⁵ K. Dziewonski and C. Paschalski, *ibid.*, 1913, **46**, 1986; 1914, **47**, 2680; *A.*, 1913, i, 847; 1915, i, 229.

³⁶ N. A. Rosanov, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 591; *A.*, i, 657.

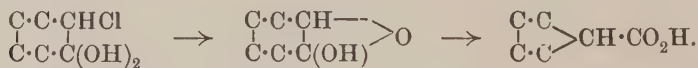
The iodohydrin of *cyclohexanediol* when treated with silver nitrate yields *cyclopentanal*,³⁷ but the reaction takes a different



course with certain homologues of the iodohydrin. Thus, 2-iodo-1-phenyl-4-methyl*cyclohexan*-1-ol (I) yields 1-phenyl-3-methyl*cyclohexan*-6-one (III), 1-phenyl-5-methyl- Δ^1 -*cyclohexen*-2-ol (II) being formed as an intermediate product.³⁸



Cyclic α -chloroketones are converted on treatment with alcoholic potassium hydroxide into cyclic acids with the number of carbon atoms in the ring diminished by one. Thus, 2-chloro*cyclohexanone* yields *cyclopentanecarboxylic acid*. The carboxyl group is always found at the carbon atom to which the chlorine atom is united in the chloroketone, and the following scheme may represent the change: ³⁹

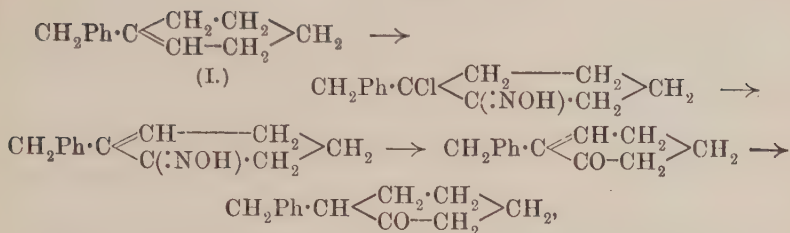


Two interesting researches carried out in each case to determine the position of an unsaturated linking may be noted. It has been found that 1-benzyl*cyclohexan*-1-ol and phenyl*cyclohexylcarbinol* yield the same hydrocarbon on dehydration. The specific refraction of this substance favours the view that it has the configuration of 1-benzyl- Δ^1 -*cyclohexene* (I) and not of benzyliden*cyclohexane* (II), which contains a conjugated double linking. Chemical evidence to the same end has now been adduced. The nitrosochloride of the hydrocarbon was converted into the oxime. This was hydrolysed to the ketone and the latter reduced. 1-Benzyl- Δ^1 -*cyclohexene* should yield 1-benzyl*cyclohexan*-2-one by this treatment:

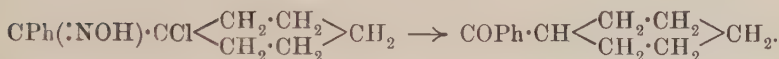
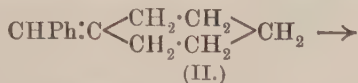
³⁷ M. Tiffeneau, *Compt. rend.*, 1914, **159**, 771; *A.*, i, 12.

³⁸ M. Le Brazidec, *ibid.*, 774; *A.*, i, 12.

³⁹ A. Favorski and V. Boshovski, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1097; *A.*, i, 411.

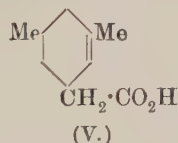
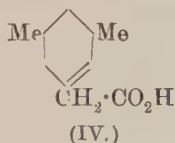
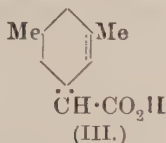


whilst benzylidenecyclohexane should yield benzoylcyclohexane,



Actually, the final product is not identical with benzoylcyclohexane, and is therefore assumed to be 1-benzoylcyclohexan-2-one.⁴⁰

The reduction of 1:3-dimethyl- Δ^3 -cyclohexenylidene-5-acetic acid (III) might lead either to 1:3-dimethyl- Δ^4 -cyclohexenyl-5-acetic acid (IV) if the substance behaves as an $\alpha\beta\gamma\delta$ -unsaturated acid or to the Δ^3 -acid (V) if the semicyclic linking becomes reduced before the endocyclic linking. It has now been shown that reduction



leads to the acid (IV).⁴¹

The oxidation of alicyclic carbinols and aldehydes with nitric acid leads to the formation of dibasic fatty acids with the same number of carbon atoms in the molecule as were contained in the ring; thus, cyclohexylcarbinol and cyclohexanealdehyde yield adipic acid. The alicyclic acids, however, in this case cyclohexanecarboxylic acid, are practically unattacked by nitric acid, and cannot therefore be regarded as intermediate products in the degradation of the carbinols and aldehydes.⁴²

The action of dilute nitric acid on the three bicyclic hydrocarbons camphane (I), camphenilane (II), and isocamphane (III) has been studied.⁴³ Camphane yields a mixture of α - and α' -nitro-

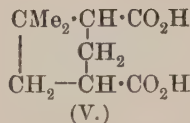
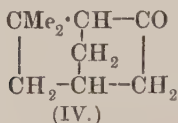
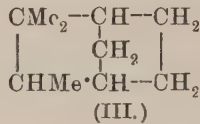
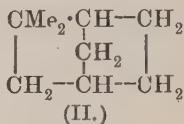
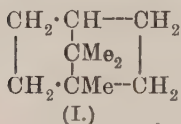
⁴⁰ K. von Auwers and W. Treppmann, *Ber.*, 1915, **48**, 1207; *A.*, i, 789.

⁴¹ K. von Auwers and W. Treppmann, *ibid.*, 1377; *A.*, i, 1058.

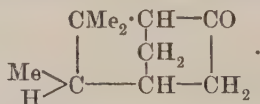
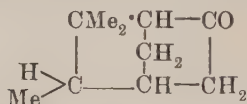
⁴² S. S. Nametkin and Mlle. A. K. Rushenceva, *J. Russ. Phys. Chem. Soc.* 1914, **46**, 1540; *A.*, i, 513.

⁴³ S. S. Nametkin and collaborators, *ibid.*, 1915, **47**, 405, 409, 414, 425; *A.*, i, 698, 699, 700, 701.

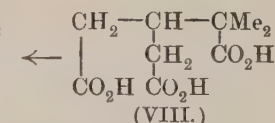
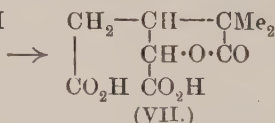
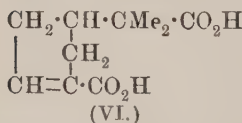
camphane and camphoric acid. Camphenilane yields β -nitrocamphenilane, β -isocamphenilone (IV), and 4:4-dimethylcyclo-



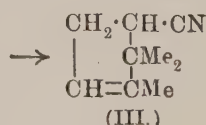
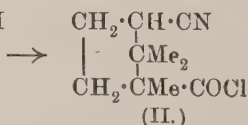
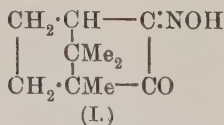
pentane-1:3-dicarboxylic acid (V). *iso*Camphane yields a mixture of stereoisomeric nitro-compounds, which on oxidation with permanganate gives two isomeric ketones, termed *isocamphones*. These are probably β - and β' -*isocamphones*, having the formulæ



Dehydrocamphenic acid (VI) yields on oxidation with nitric acid a lactone-dicarboxylic acid, $\text{C}_9\text{H}_{12}\text{O}_6$, for which several different formulæ have been proposed (O. Aschan, W. N. Haworth, and A. T. King,⁴⁴ P. Lipp,⁴⁵). P. Lipp⁴⁶ has now synthesised the lactonic acid and a stereoisomeride by the action of bromine on *isocamphoric* acid (VIII), and thus confirmed the formula (VII) which he assigned to it previously.



Distillation of oximinocamphor (I) with phosphorus pentachloride leads to cyanolauronyl chloride (II), but a portion of this compound suffers loss of carbon monoxide and hydrogen chloride in the course of the reaction and passes into camphoceenonitrile (III).⁴⁷



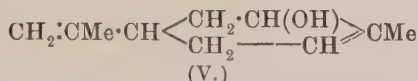
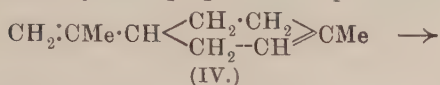
⁴⁴ *Ann. Report*, 1912, 149; 1913, 119.

⁴⁵ *Ibid.*, 1914, 119; *Ber.*, 1914, 47, 871; *A.*, 1914, i, 542.

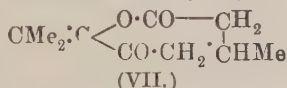
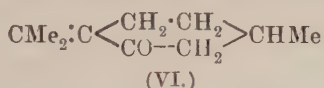
⁴⁶ *Ibid.*, 2994; *A.*, i, 553.

⁴⁷ W. Borsche and W. Sander, *ibid.*, 1915, 48, 117; *A.*, i, 148.

Several papers have appeared on the autoxidation of terpenes. Limonene (IV)⁴⁸ gives a mixture of products, amongst which are found carvone and carveol (V). The latter substance had not previously been prepared in a pure state.



Pulegone (VI) yields acetone, β -methyladipic acid, and a ketolactone, which probably has the constitution (VII),⁴⁹ whilst



citronellaldehyde⁵⁰ gives a large number of degradation products.

The Organic Compounds of Selenium.

Several new methods for the introduction of selenium into the nucleus of aromatic compounds have been described in the last few years. The most important is an adaptation of the methods of Sandmeyer and Gattermann. Potassium selenocyanate is added to a solution of a diazonium salt which has been neutralised to Congo-red paper by means of sodium acetate. The aryl selenocyanate, $\text{R}\cdot\text{SeCN}$, thus formed is readily converted by means of alkali into the selenol, $\text{R}\cdot\text{SeH}$, which becomes spontaneously oxidised in the air to the diaryl diselenide, $\text{RSe}\cdot\text{SeR}$.⁵¹ Somewhat similar is the preparation of a mixture of diaryl diselenide, R_2Se_2 , and diaryl selenide, R_2Se , by the action of potassium diselenide, K_2Se_2 , on diazonium salts.⁵² Compounds with a labile halogen atom, such as *o*-chloronitrobenzene, react with sodium hydrogen selenide⁵³ or potassium selenocyanate⁵⁴ to give aryl selenols or aryl selenocyanates. Selenium and its chlorides combine with diphenylamine on heating to give selenodiphenylamine.⁵⁵

⁴⁸ A. Blumann and O. Zeitschel, *Ber.*, 1914, **47**, 2623; *A.*, i, 426.

⁴⁹ E. Sernagiotto, *Atti R. Accad. Lincei*, 1915, [v], **24**, i, 1065; *A.*, i, 826.

⁵⁰ E. Sernagiotto, *ibid.*, 850; *A.*, i, 889.

⁵¹ H. Bauer, *Ber.*, 1913, **46**, 92; *A.*, 1913, i, 263; G. T. Morgan and J. C. Elliot, *P.*, 1914, **30**, 248.

⁵² R. Lesser and R. Weiss, *ibid.*, 1912, **45**, 1835; 1913, **46**, 2640; 1914, **47**, 2292, 2505; *A.*, 1912, i, 642; 1913, i, 1184; 1914, i, 1083; 1915, i, 404.

⁵³ H. Bauer, *loc. cit.*

⁵⁴ E. Fromm and K. Martin, *Annalen*, 1913, **401**, 177; *A.*, 1913, i, 1323.

⁵⁵ C. Weizmann and H. Stephens, *P.*, 1913, **29**, 196; W. Cornelius, *J. pr. Chem.*, 1913, [ii], **88**, 395; *A.*, 1913, i, 1090.

Selenic acid reacts with benzene and toluene to give arylselenious acids, in the latter case ortho- and para-substituted derivatives being formed,⁵⁶ but aniline selenate does not yield *p*-aminophenylselenious acid on heating in the same way that aniline sulphate and arsenate yield sulphanilic and arsanilic acids,⁵⁷ for the acid is reduced to selenium.

The action of Grignard's reagent on the chlorides of selenium has given interesting results. It was shown some years ago⁵⁸ that elementary sulphur or selenium readily react with this reagent, giving thiophenol and diphenyl disulphide, or the corresponding selenium analogues. Incidentally, it may be remarked that this is a very convenient method for the preparation of diphenyl diselenide. Sulphur chloride also yields the disulphides with magnesium phenyl or benzyl haloids, whilst thionyl chloride gives the sulphoxides with the same reagents.⁵⁹ Selenium dichloride, however, whilst yielding with magnesium phenyl bromide the normal product diphenyl diselenide together with some diphenyl selenide, behaves abnormally with magnesium benzyl chloride, giving besides the normal product, dibenzyl diselenide, a considerable quantity of dibenzyl selenodichloride, $\text{Se}(\text{C}_7\text{H}_7)_2\text{Cl}_2$. This product presumably results from the decomposition of selenium dichloride into selenium and selenium tetrachloride, for the latter compound yields the same product with magnesium benzyl chloride. The products obtained from selenyl chloride are not analogous to those prepared from thionyl chloride, for they do not contain oxygen; magnesium phenyl bromide gives diphenyl selenide, and magnesium benzyl chloride gives dibenzyl selenodichloride.⁶⁰ The action of selenium bromide on magnesium alkyl and aryl haloids has also been studied.⁶¹

The Organic Compounds of Arsenic.

The development of this branch of organic chemistry down to the preparation of salvarsan, 4:4'-dihydroxy-3:3'-diaminoarsenobenzene dihydrochloride, was ably reviewed in the Annual Reports for 1911. Since then the importance of salvarsan as a remedy for syphilis has led to an enormous amount of work on aromatic arsenic

⁵⁶ H. W. Doughty, *Amer. Chem. J.*, 1909, **41**, 326; H. W. Doughty and F. R. Elder, *Eighth Inter. Cong. App. Chem.*, 1912, **6**, 93; *A.*, 1909, i, 296; 1913, i, 962.

⁵⁷ F. L. Pyman, *P.*, 1914, **30**, 302.

⁵⁸ H. Wuyts and G. Cosyns, *Bull. Soc. chim.*, 1903, [iii], **29**, 689; F. Taboury, *ibid.*, 1903, [iii], **29**, 761; 1906, [iii], **35**, 668; *A.*, 1903, i, 686, 748; 1906, i, 834.

⁵⁹ W. Strecker, *Ber.*, 1910, **43**, 1131; *A.*, 1910, i, 532.

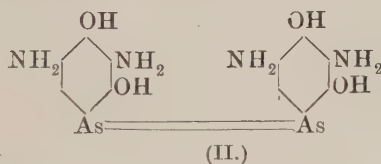
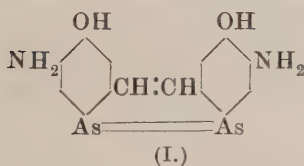
⁶⁰ W. Strecker and A. Willing, *ibid.*, 1915, **48**, 196; *A.*, i, 238.

⁶¹ A. Pieroni and C. Coli, *Gazzetta*, 1914, **44**, ii, 349; A. Pieroni and G. Balduzzi, *ibid.*, 1915, **45**, ii, 106; *A.*, 1914, i, 1198; 1915, i, 956.

compounds. Salvarsan is chiefly administered by intravenous injection, and for this purpose the aqueous solution of the salt, which is strongly acid, has to be mixed with sufficient sodium hydroxide to neutralise the hydrochloric acid and redissolve the insoluble base as phenoxide. This procedure, which requires care and skill to give a sterile solution, is undertaken unwillingly by many medical men, and in any case gives an alkaline solution. Many attempts have therefore been made to supersede salvarsan by some derivative that would be immediately soluble in water, giving a neutral solution, and equally efficacious in the treatment of disease. This work led to the preparation of many simple derivatives of salvarsan, such as neosalvarsan, a condensation product of salvarsan with sodium formaldehydesulphoxylate, in which one of the amino-groups of the original product becomes $\cdot\text{NH}\cdot\text{CH}_2\cdot\text{SO}_2\text{Na}$. It is readily soluble in water and neutral, but opinions differ as to its therapeutic value compared with salvarsan.

A great number of substituted arsenobenzenes, many of them substituted salvarsans, have been prepared during the period under review (1912—1915), but none has been found to be an improvement on this substance.

Amongst the substituted salvarsans we may note the *N*-dimethyl and *N*-tetramethyl derivatives, which are ten times as toxic as salvarsan; and the *N*-hexamethyldiammonium salts, which are three to five times as toxic,⁶² 5:5'-diaminosalvarsan and its di-*o*-methyl ether,⁶³ a stilbene derivative of salvarsan⁶⁴ (I),



6:6'-dihydroxysalvarsan, and 5:5'-diamino-6:6'-dihydroxysalvarsan (II), which have an augmented toxicity but no corresponding therapeutic value,⁶⁵ and the two isomeric 5:5'- and 6:6'-dicarboxylic acids derived from salvarsan.⁶⁶

An important new general method for the synthesis of aromatic arsinic acids is the replacement of the amino-group of an aromatic amine by $\cdot\text{AsO}(\text{OH})_2$. This operation is easily carried out by adding the diazotised solution of the amine to a solution of sodium

⁶² A. Bertheim, *Ber.*, 1912, **45**, 2130; *A.*, i, 818.

⁶³ P. Karrer, *ibid.*, 1914, **47**, 2275; *A.*, 1914, i, 1100.

⁶⁴ P. Karrer, *ibid.*, 1915, **48**, 305; *A.*, i, 333.

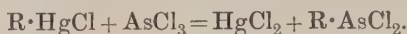
⁶⁵ H. Bauer, *ibid.*, 509; *A.*, i, 606.

⁶⁶ P. Karrer, *ibid.*, 1058; *A.*, i, 855.

arsenite and heating the mixture with sodium hydroxide. The yield is about 30 per cent. of the theoretical.⁶⁷



Another new method for the introduction of arsenic into the para-position of a substituted benzene derivative is announced. Benzene derivatives are readily converted into chloromercuri-compounds, $\text{R}\cdot\text{HgCl}$, in which the chloromercuri-group occupies a position para to that of the substituent in the benzene nucleus, and it has now been found that the chloromercuri-compounds readily yield dichloroarsines when heated with arsenic trichloride.

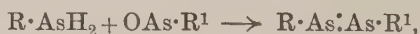


The reaction is surprising, since the similarly constituted magnesium alkyl haloids give only tertiary arsines with arsenic trichloride.⁶⁸

A change in the reverse direction is effected by treating aromatic compounds containing tervalent arsenic with mercuri-salts in aqueous solution, when mercury diaryls and arsenious acid are formed.⁶⁹

Other important new methods in this field are as follows.

The reduction of an equimolecular mixture of two aromatic arsinic acids, $\text{R}\cdot\text{AsO}(\text{OH})_2$ and $\text{R}^1\text{AsO}(\text{OH})_2$, leads to the formation of an asymmetrical arsenobenzene, $\text{R}\cdot\text{As}\cdot\text{As}\cdot\text{R}^1$.⁷⁰ Hypophosphorous acid is a specific reducing agent for the arsinic acid group, so that aromatic arsinic acids containing a nitro- or azo-group can be reduced by this acid to arsenobenzenes still containing these groups.⁷¹ The reduction of aromatic arsinic acids with metals and mineral acids leads to the arsines, $\text{R}\cdot\text{AsH}_2$,⁷² which may be condensed with (a) arylarsenious oxides or haloids to give arsenobenzenes: ⁷³



or (b) with antimony trichloride, substituted stibine dichlorides, or bismuth trichloride to give the compounds $\text{R}\cdot\text{As}\cdot\text{SbCl}$, $\text{R}\cdot\text{As}\cdot\text{Sb}\cdot\text{R}$, and $\text{R}\cdot\text{As}\cdot\text{BiCl}$ respectively.⁷⁴

Aromatic arsine dichlorides, $\text{R}\cdot\text{AsCl}_2$, combine with phosphorus,

⁶⁷ H. Bart, D.R.-P., 250264; *A.*, 1913, i, 115.

⁶⁸ G. Roeder and N. Blasi, *Ber.*, 1914, 47, 2748; *A.*, i, 331.

⁶⁹ D.R.-P., 272289; *A.*, i, 34.

⁷⁰ D.R.-P., 251104; *A.*, 1913, i, 116.

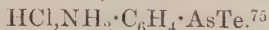
⁷¹ P. Karrer, *Ber.*, 1914, 47, 2275; *A.*, 1914, i, 1100.

⁷² D.R.-P., 251571; *A.*, 1913, i, 117.

⁷³ D.R.-P., 254187; *A.*, 1913, i, 416.

⁷⁴ P. Ehrlich and P. Karrer, *Ber.*, 1913, 46, 3564; *A.*, 1914, i, 99.

arsenic, antimony, selenium, and tellurium hydrides, forming condensation products, such as, in the last case,

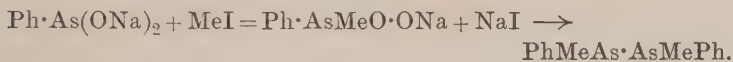


Arsenobenzenes also yield additive compounds with the salts of the noble metals.⁷⁶

The methylation of arsenobenzenes and arylarsenious oxides leads to interesting results. The former suffer fission when heated with methyl iodide, giving an arylarsonium iodide and an arylarsine di-iodide.⁷⁷



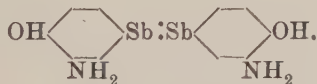
Aromatic arsenious oxides combine with alkyl haloids in the presence of alkali, yielding arylalkylarsinic acids, which on reduction yield diaryldialkyldiarsines,



4 : 4'-Dihydroxy-3 : 3'-diaminodiphenyldimethyldiarsine has been made in this way; it is closely related to salvarsan, but its toxicity is greater and its therapeutic action less.⁷⁸

The Organic Compounds of Antimony.

The antimony analogue of salvarsan has been prepared by methods similar to those used for salvarsan. Monoacetyl-*p*-phenylenediamine is diazotised and mixed with sodium antimonite, yielding *p*-acetylaminostibinic acid. This is nitrated and the product hydrolysed, when 3-nitro-4-hydroxyphenyl-1-stibinic acid is formed. Reduction of the nitro-acid with sodium hyposulphite results in the formation of 4 : 4'-dihydroxy-3 : 3'-diaminostibino-benzene.⁷⁹



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⁷⁵ D.R.-P., 269699; *A.*, 1914, i, 609.

⁷⁶ D.R.-P., 268220, 268221; P. Ehrlich and P. Karrer, *Ber.*, 1915, **48**, 1634; *A.*, 1914, i, 345; 1916, i, 95.

⁷⁷ A. Bertheim *ibid.*, 1914, **47**, 271; *A.*, i, 344.

⁷⁸ A. Bertheim, *ibid.*, 1915, **48**, 350; *A.*, i, 331.

⁷⁹ D.R.-P., 254421, 259875, 268451; *A.*, 1913, i, 416, 1122; 1914, i, 216.

PART III.—HETEROCYCLIC DIVISION.

LAST year the outbreak of the war rendered it impossible to survey the contents of the German and Austrian journals beyond July, so that in the present Report it has been considered advisable to deal with certain papers which in point of date actually belong to an earlier volume. In this way it is hoped that the Report, although technically incorrect in its title, will nevertheless serve a more useful purpose than it would have done had the materials standing over from last year been omitted entirely from the review.

It must be admitted that, even with this addition, the material which the writer had at his disposal is not of a character that lends itself to interesting treatment. It is true that the chemistry of the anthocyanins has progressed very rapidly since the last Annual Report was published, but the development in this field has been largely a matter of steady progress in detail rather than an advance in main principles; and as a result, although the new knowledge thus gained is of the greatest importance, it does not conduce to the production of a readable narrative.

The chemistry of chlorophyll had already begun to show a decline in the period covered by last year's Report, and since Willstätter has turned his energies in another direction it is unlikely that we shall see in the immediate future any further flow of connected researches like those which were published in the last five years. Investigation is going on, but it is improbable that it will be conducted on the same gigantic scale.

The pigments of the blood and of the bile still furnish a steady stream of contributions to our knowledge, although it must be admitted that the difficulties of following the trend of discovery in this line are greatly increased by two factors, namely, the continual changing of nomenclature and the violent polemics in which the various investigators indulge. The subject is one of intense difficulty, both on the experimental side and in the deduction of probable conclusions from the multitude of perplexing data which are brought to light, and it seems regrettable that investigators who are engaged in such laborious and important researches cannot avoid the waste of time and energy which these controversies entail both on their authors and on those who are following their work.

Our knowledge of the alkaloids has not increased much on the theoretical side during the current year, but a vast amount of information is being accumulated with regard to new and little known compounds of this class. This side of the subject appears

to have taken a fresh lease of life, and numerous investigators are turning their attention to it.

Compounds containing a pyrone nucleus have attracted a considerable amount of attention during the period under review, and in this region of the subject there seems to be considerable scope for work along the lines which have been struck out by various workers.

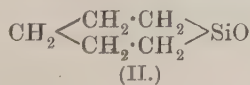
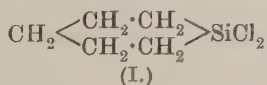
Some new heterocyclic compounds have been synthesised in which atoms of silicon, arsenic, and titanium are present as members of the rings. Among the nitrogen compounds, also, considerable advances in our knowledge have been made, and the synthesis of silver pentazole, although strictly speaking it belongs rather to inorganic than to organic chemistry, has furnished us with a most remarkable example of the aptitude with which nitrogen atoms lend themselves to the formation of cyclic compounds.

Apart from these subjects, there is, of course, a vast amount of material which a Reporter cannot utilise owing to the exigencies of space; and a general survey of the papers published shows that there is no sign of the heterocyclic section of organic chemistry failing in its attraction for numerous workers.

Some New Heterocyclic Types.

The chemistry of the heterocyclic compounds has of recent years tended more and more towards the building up of extremely complex rings, and it is rather a relief to find that this year one or two substances of much simpler character have furnished materials for research. Of these, the most interesting is a cyclic compound which contains a silicon atom among the members of the ring. Hitherto, cyclic silicon compounds have not been very closely examined. Some have been obtained¹ by the action of sodium on a mixture of silicon tetrachloride and trimethylene bromide (or *o*-dichlorobenzene), but the compounds resulting from this reaction were of a somewhat indefinite nature. The application of the Grignard reagent has led to the synthesis of more satisfactory substances,² and the heterocyclic chemistry of silicon seems to be on the verge of an interesting advance.

When a Grignard reagent obtained from α -dibromopentane is allowed to react with silicon tetrachloride, *cyclopentamethylene*-

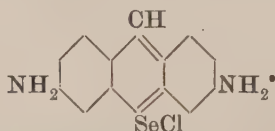


¹ Hart, *Brit. Assoc. Rep.*, 1887, 661.

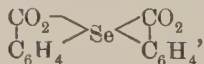
² A. Bygdén, *Ber.*, 1915, 48, 1236; *A.*, i, 912.

silicon dichloride (I) is produced, which is hydrolysed by water to form a polymeride of *cyclopentamethylenesilicone* (II). When dimethylsilicon dichloride is substituted for silicon tetrachloride in the first reaction, the end-product contains the methyl groups in place of the two chlorine atoms of formula I, and has been termed *dimethylcyclopentamethylenesilicane*.

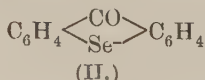
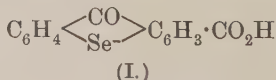
The preparation of a simple six-membered selenium derivative of the heterocyclic series has been undertaken³ with the object of testing the properties of the new substance from the point of view of a dye, and also, ultimately, as a drug in the treatment of trypanosomiasis. In neither respect has the compound been satisfactory, so that its chief interest is purely chemical. The outline of the method employed to prepare it is as follows. *pp'*-Diaminodiphenylmethane is acetylated, nitrated, and reduced. The resulting *oo'*-diamino-*pp'*-diacetyldiaminomethane is diazotised and then treated with potassium selenoselenate. By means of concentrated sulphuric acid the acetyl radicles are eliminated, and the end-product of the reaction is found to be 3:6-diaminoselenopyronine, which is isolated in the form of its chloride:



Rather more complex than this is a substance which was originally supposed to be benzophenoneselenone, but has now been shown to be a dilactone⁴ derived from a hypothetical diphenylselenoxide, di-*o*-carboxylic acid or from the corresponding dihydroxy-compound, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{Se}(\text{OH})_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. The structure of the dilactone appears now to be established as



so that it is an example of a heterocyclic substance somewhat akin in type to the spirans. Various derivatives of selenoxanthone-



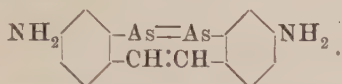
carboxylic acid (I) have also been examined, and selenoxanthone itself (II) has been obtained by heating the acid with lime.

The pharmacological value of arsenic has led, in recent years, to a very careful study of the arsenic derivatives, and in the present

³ P. Ehrlich and H. Bauer, *Ber.*, 1915, **48**, 502; *A.*, i, 579.

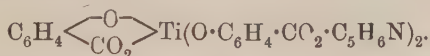
⁴ R. Lesser and R. Weiss, *ibid.*, 1914, **47**, 2510; *A.*, i, 445.

year a new type of heterocyclic derivative has been obtained⁵ which contains two arsenic atoms in the ring. By acting on 5-nitro-2-methylphenylarsinic acid with sodium hydroxide, dyes are obtained which, when reduced in alkaline solution, yield 5:5'-diamino-2:2'-stilbenediarsinic acid, and from this compound, by means of hyposulphite, it is possible to produce 5:5'-diamino-1:1'-arseno-2:2'-stilbene:

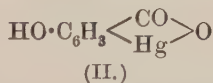
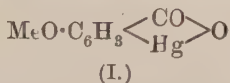


Derivatives of this substance have been prepared, but the physiological result of their action is apparently disappointing.

One or two titanium derivatives⁶ might be regarded as coming within the limits of this section of the subject. When titanium tetrachloride is treated with various organic acids, compounds are produced which apparently contain a titanium atom as a member of a ring. Thus, when salicylic acid reacts with titanium tetrachloride, a compound is formed which, when treated with pyridine in alcoholic solution, produces a salt, formulated by Rosenheim thus:



Salicylic acid plays a part in the formation of another heterocyclic substance the ring of which contains a metallic atom.⁷ When sodium *p*-methoxybenzoate reacts in aqueous solution with a mercuric salt, the corresponding mercury salt is produced, which appears to have the structure $(\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_2\text{Hg}$. On boiling with water, this substance is converted into a new compound which does not show any of the ordinary reactions of mercury, and its formula is therefore supposed to be I. Since this substance



is produced without the intervention of any hydroxyl radicle (the hydroxyl of the acid being methylated), and since a perfectly analogous reaction occurs when salicylic acid itself is employed instead of its methyl ether, it seems reasonable to assume that the substance derived from salicylic acid has the structure shown in II.

Rather more complex than any of the foregoing is the new sub-

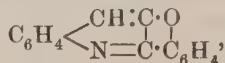
⁵ P. Karrer, *Ber.*, 1915, **48**, 305; *A.*, i, 333.

⁶ A. Rosenheim, *ibid.*, 447; *A.*, i, 537.

⁷ H. Lajoux, *J. Pharm. Chim.*, 1915, [vii], **11**, 279; *A.*, i, 537.

⁸ R. Stoermer and E. Barthelmes, *Ber.*, 1915, **48**, 502; *A.*, i, 152.

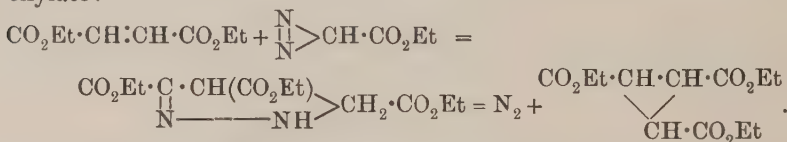
stance coumarinoline, which is, produced by the reduction of *o*-nitrobenzylidenecoumarone with sodium hyposulphite in aqueous-alcoholic solution. The reduction leads to the formation of the corresponding amino-derivative, but this at once undergoes intramolecular rearrangement, with the formation of the substance



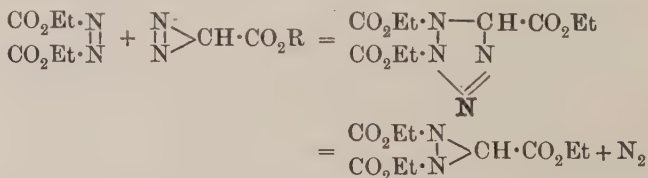
which has received the name coumarinoline, on account of its kinship with quindoline and thioquindoline.

Some Derivatives of Hydraziacetic Acid.

It will be remembered that ethyl diazoacetate and ethyl fumarate interact with the formation of the triethyl ester of pyrazolinetricarboxylic acid, and that the latter compound, when heated, evolves nitrogen and yields ethyl trimethylenetricarboxylate:



An analogous reaction has been observed when ethyl fumarate is replaced by ethyl azodicarboxylate,⁹ but in this case the first product is a heterocyclic compound containing four nitrogen atoms in its nucleus, whilst the end-product of the reaction is a derivative of the true hydraziacetic acid:

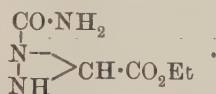
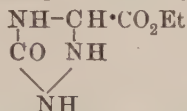


This reaction takes place in alcoholic solution; but if the two reagents be permitted to interact without any diluent, and if, at the same time, the reaction temperature does not exceed 120°, a totally different product is obtained. This new compound has the composition $\text{C}_5\text{H}_9\text{O}_3\text{N}_3$, and when it is hydrolysed it yields hydrazine, ammonia, and glyoxylic acid. One possible formula for such a substance is $\text{NH}_2 \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, and when a compound of this structure was synthesised its properties were found to be identical with those of the product obtained from ethyl diazo-

⁹ E. Müller, *Ber.*, 1914, **47**, 3001; *A.*, i, 509.

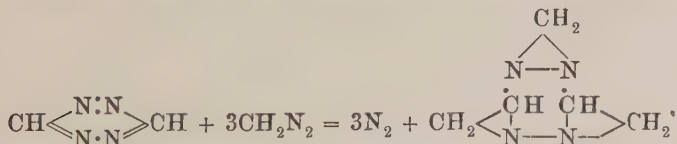
acetate and ethyl azodicarboxylate, so that the constitution is definitely established.

A variation was introduced into the procedure by replacing the ethyl azodicarboxylate by azodicarbonamide, with the object of preparing an amide of hydrazimethanetricarboxylic acid; but this method did not yield the results which had been expected. The end-product of the reaction was found to be isomeric with the compound obtained in the previous case, but its hydrolysis products are different. When treated with concentrated hydrochloric acid in a sealed tube, it yielded alcohol, carbon dioxide, ammonia, hydrazine, and glyoxylic acid; hydrolysis with dilute sulphuric acid gave rise to the semicarbazone of glyoxylic acid, and when the substance was merely boiled with water, it yielded the semicarbazone of ethyl glyoxylate. From these data it seems probable that the compound has either of the structures shown below, the right-hand one being the more probable of the two:



Azodibenzoyl, when treated with ethyl diazoacetate, yields as the end-products of the reaction ethyl dibenzoylhydrazacetate, $\begin{array}{c} \text{NBz} \\ | \\ \text{NBz} \end{array} > \text{CH}\cdot\text{CO}_2\text{Et}$, and a small quantity of tribenzoylhydrazine.

Much more complicated is the substance which results when 1:2:4:5-tetrazine is treated with diazomethane. Here three molecules of diazomethane react, and three molecules of nitrogen are eliminated with the final formation of trimethylenetetrazine:



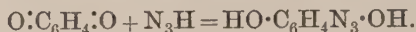
which, on hydrolysis with dilute sulphuric acid, decomposes into formaldehyde and hydrazine.

Azoimide and its Derivatives.

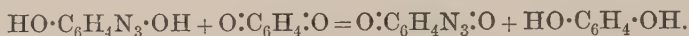
The action of azoimide on *p*-benzoquinone¹⁰ appears to be much more complicated than might have been expected at first sight. The earliest stage seems to be the attachment of the azoimide nucleus to the quinone nucleus, followed by the reattachment of

¹⁰ E. Oliveri-Mandalà and E. Calderaro, *Gazzetta*, 1915, 45, 307; *A.*, i, 909; E. Oliveri-Mandalà, *ibid.*, ii, 120; *A.*, i, 1013.

the two hydrogen atoms (one from the azoimide and one from the quinone nucleus) to the oxygen atoms of the quinone:



The second stage consists of an interaction between the new compound and a second molecule of *p*-benzoquinone, which becomes reduced to quinol:



The quinol then attacks a third molecule of *p*-benzoquinone to form quinhydrone. The fourth stage in the reaction is furnished by an interaction between this quinhydrone and a second molecule of azoimide which produces quinol and the compound $\text{HO}\cdot\text{C}_6\text{H}_4\text{N}_3\cdot\text{OH}$. A fifth reaction occurs between quinol and the compound $\text{O}:\text{C}_6\text{H}_4\text{N}_3:\text{O}$, with the formation of *p*-benzoquinone and

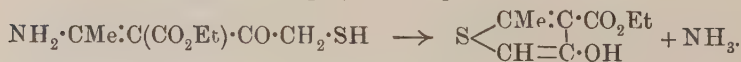


Thus the end-products of the series of reactions are quinhydrone and the azide of quinol.

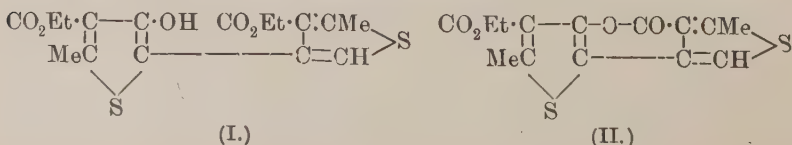
Triazoquinol, $\text{HO}\cdot\text{C}_6\text{H}_4\text{N}_3\cdot\text{OH}$, is quite stable towards shock, but explodes violently when heated. When heated with aqueous alcohol or treated with cold acid or alkali, it yields nitrogen and azoimide. With ammonia solution, it gives a green coloration, which changes to red, nitrogen being evolved.

The Thiophen Group.

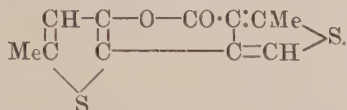
When ethyl β -aminocrotonate is allowed to react with chloroacetyl chloride it forms ethyl β -amino- α -chloroacetyl crotonate, and it has now been found that the action of potassium hydrosulphide on this ester yields a hydroxythiophen derivative.



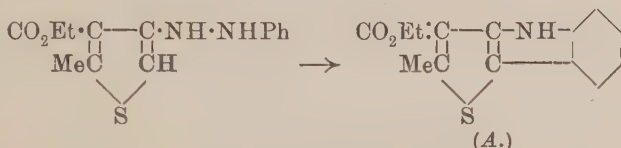
The hydrogen atom in the position 2 is very reactive, and in consequence of this the substance has been found capable of undergoing various condensations. Thus, in the presence of concentrated hydrochloric acid two molecules of the ester take part in a reaction which leads to the formation of ethyl 3-hydroxy-5:5'-dimethylbis-2:3'-thiophen-4:4'-dicarboxylate (I):



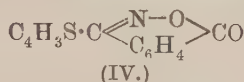
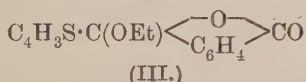
The corresponding acid yields a lactone of the structure II, and when this lactone is distilled with lime the lactone of a new acid is produced, which has the structure



The original ester reacts with formaldehyde, giving a compound of the type (A), whilst benzaldehyde yields an analogous substance. With phenylhydrazine a phenylhydrazino-derivative is produced, which undergoes condensation in the presence of warm acetic acid: Further reactions of the substance are described in the original paper.¹¹



The action of phthalic anhydride on thiophen in the presence of aluminium chloride leads to the production of *o*-2-thienoylbenzoic acid,¹² $\text{C}_4\text{H}_3\text{S}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. This substance forms two isomeric esters, for in addition to the ethylation of the carboxyl group in the normal manner a second type of reaction leads to the production of a ψ -ester having the structure III. The ψ -ester reacts with



alcoholic ammonia to form the corresponding ψ -amide, but the normal ester does not appear to react with ammonia at all. With hydroxylamine hydrochloride and aqueous potassium hydroxide *o*-thienoylbenzoic acid yields an anhydro-oxime which has the structure IV, whilst thiophenanthraquinone can be obtained from the acid by the action of phosphoric oxide or concentrated sulphuric acid.

Some further study of the thianthren group has been made, but the results are such as to make reference to the original necessary.¹³

Some Condensation Reactions of o-Thiolbenzoic Acid.

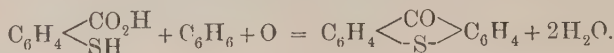
Compounds containing the keto-methylene group lend themselves with readiness to certain types of reaction, and during the present

¹¹ E. Benary and A. Baravian, *Ber.*, 1915, **48**, 593; *A.*, i, 576.

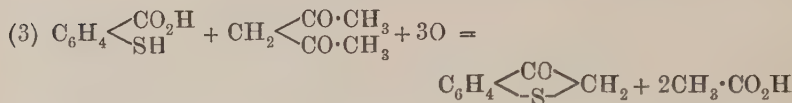
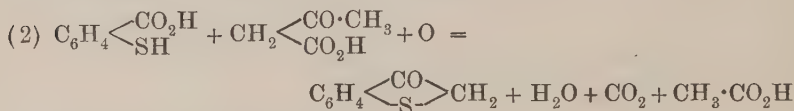
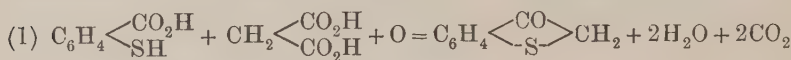
¹² W. Steinkopf, *Annalen*, 1914, **407**, 94; *A.*, i, 155.

¹³ K. Fries and E. Engelbertz, *ibid.*, 194; *A.*, i, 155.

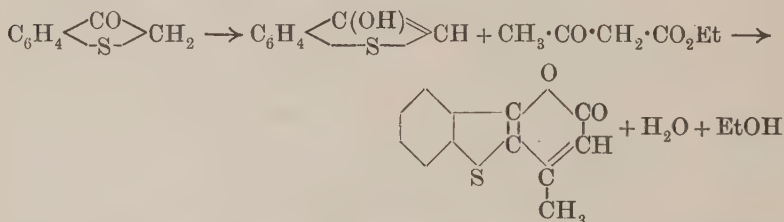
year a fresh field has been opened in this section of the subject.¹⁴ It will be recalled that *o*-thiolbenzoic acid has already been found susceptible to many condensation reactions, such as that which leads to the formation of thioxanthone:



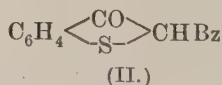
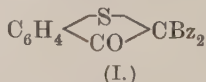
Further investigations have now been made, in which aliphatic derivatives are substituted for the aromatic compounds, and the results may be expressed concisely in the following equations:



In the case of the second reaction another product is usually formed along with 3-oxy(1)thionaphthen, as the reaction may proceed further, as indicated by the formulæ below:



With *o*-thiolbenzoic acid, dibenzoylmethane yields 2:2-dibenzoyl-3-oxy(1)thionaphthen (I), whilst benzoylacetone produces 2-benzoyl-3-oxy(1)thionaphthen (II), the latter of which can readily be converted into "thioindigo":



Analogous condensations take place between *o*-thiolbenzoic acid and other ketomethylene derivatives, but the course of the reaction is not always so simple as those shown above.

¹⁴ S. Smiles and B. N. Ghosh, *T.*, 1915, **107**, 1377.

Pyrrole and its Allies.

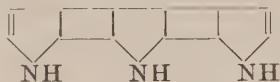
A considerable amount of work has been carried out on the pyrrole group during the period under review, and some of it appears worthy of notice. It is well known that pyrrole derivatives under certain conditions are peculiarly liable to undergo intramolecular rearrangement, and any investigations which throw light on this point are of value. The reactions of the metallic derivatives of pyrrole are rendered somewhat obscure owing to the fact that our knowledge of their exact mode of reaction is still rather vague, and the work which has been carried out on the isomerism of the organo-metallic compounds of pyrrole under the action of ethyl chlorocarbonate and ethyl carbonate deserve examination. Potassio-pyrrole yields differently substituted pyrrole derivatives according to the reagent used to replace the potassium atom. Thus with alkyl iodides it gives mainly 1-pyrrole derivatives; with the chloroanhydrides of acids the yield is made up of 1- and 2-derivatives in almost equal proportions, whilst the action of anhydrides furnishes 2-derivatives as the chief product. This behaviour may be explained on either of two assumptions, for we may assume that in all cases a 1-compound is produced which under the conditions of reaction may be transformed to a greater or less extent into a 2-derivative, or we may suppose that the 2-compounds are formed by a single reaction and that no intermediate stage exists in the reaction. Now, in the case of the Grignard reagent, it is necessary to assume that if isomerisation takes place at all it must occur before the magnesium atom is removed from the molecule, and this might lead us to the deduction that the organo-metallic complex always enters the pyrrole nucleus in the 2-position. This view, however, has received a shock from the recent experiments with ethyl chlorocarbonate and ethyl carbonate. When magnesium pyrrol bromide reacts with the first of these compounds, the result is a 2-derivative, whereas when ethyl carbonate is used the main product is ethyl pyrrole-1-carboxylate. Thus the organo-magnesium compound behaves just like potassio-pyrrole, and it seems reasonable to suppose that both are mixtures of the 1- and 2-forms, and not homogeneous substances. Unless it is assumed that the whole magnesio-bromide radicle wanders intramolecularly, we are driven to the conclusion that the Grignard reagent attacks both the 1- and the 2-positions simultaneously.

The Grignard reagent has come into use in another section of

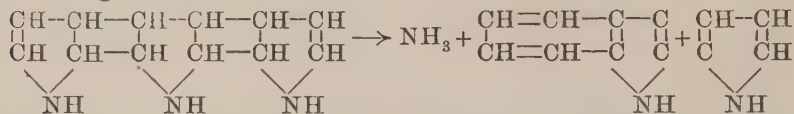
¹⁵ V. V. Tschelincev and S. G. Karmanov, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 161; *A.*, i, 297.

the pyrrole group, for it has been shown¹⁶ that this reagent furnishes a simple means of distinguishing between tertiary and secondary pyrroles. The results, which were at one time disputed, appear to be accurate, and no action takes place with tertiary compounds, whilst the secondary substances do react with the Grignard reagent.

The formation of tripyrrole by the union of three molecules of pyrrole is one of the well-known reactions in the heterocyclic series, and it has hitherto been assumed that the polymeric compound had the structure



The evidence in favour of this view may be summed up very briefly. When heated, tripyrrole decomposes into ammonia, pyrrole, and indole, a reaction which can be expressed by the following formulæ:



Further, it was found that when 2- and 3-monosubstituted pyrroles were used in place of pyrrole itself, the end-products of polymerisation were not tripyrrole derivatives, but were substances of the binary type which yielded indole derivatives when heated with sulphuric acid.

A new series of investigations¹⁷ has thrown very grave doubt on the older method of formulation; and since the subject is important from the point of view of some naturally occurring pyrrole derivatives, some account of the new work must be given in this place.

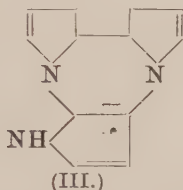
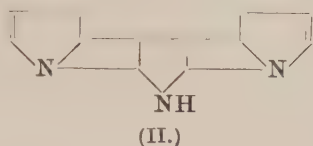
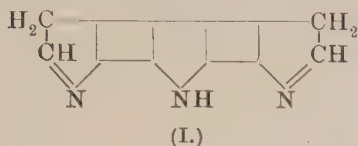
Tripyrrole hydrochloride is prepared by passing dry hydrogen chloride through a benzene solution of pyrrole. If the above formula (Dennstedt's) were correct, magnesium propyl iodide should react with tripyrrole, giving a derivative containing three MgBr residues. Actual experiment proves, however, that only one imino-hydrogen atom reacts with the Grignard reagent, so that it seems reasonable to conclude that either of two cases has presented itself. On the one hand, the reactions of the two remaining imino-groups of the Dennstedt formula may be masked in their action by some inhibitory mechanism, or on the other there may be only

¹⁶ B. Oddo, *Ber.*, 1914, **47**, 2427; *A.*, i, 451.

¹⁷ V. V. Tschelincev, B. V. Tronov, and B. I. Voskresenski, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1224; *A.*, i, 1008.

a single imino-group in the tripyrrole structure. It is safer to choose the second possibility and investigate it before examining the first.

Three structures may be suggested for tripyrrole, each of which contains only a single imino-radicle:



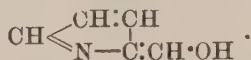
The first of these may be ruled out, as under the influence of the Grignard reagent it would probably pass by tautomeric change into the Dennstedt structure and show the reactions of three imino-radicles. The remaining two formulæ can be brought into line with the decomposition reaction of tripyrrole, with the formation of indole. The decomposition would be represented (in the case of formula II) on lines similar to those employed in the older formulation by Dennstedt, while in the case of formula III the ready decomposition of tripyrrole with the liberation of ammonia finds a close parallel in the case of the amidines. A further point in favour of the two new formulæ as against that of Dennstedt lies in the fact that tripyrrole hydrochloride contains only a single molecule of hydrogen chloride, whereas since there is no marked difference between the imino-groups of the Dennstedt structure one might reasonably expect to find either a di- or tri-hydrochloride formed by the substance.

The polymerisation of pyrrole to tripyrrole is a well-known reaction, but it was not until recently¹⁸ that any study had been made of similar condensations in the case of the trisubstituted pyrrole series. The results obtained are said to throw light on the constitution of certain pyrroles which are of interest from their relation to the bile acids. Thus, hæmopyrrole-*e* is regarded as polymerised cryptopyrrole, hæmopyrrole-*g* is supposed to be an impure phyllopyrrole, and hæmopyrrole-*f* is taken to be another dimeric form belonging to the same class.

The aldehydes of pyrrole have also been submitted to investiga-

¹⁸ H. Fischer, *Ber.*, 1915, 48, 401; *A.*, i, 460.

tion, and two methods of preparing pyrrole-2-aldehyde are described in the year's literature. Magnesium pyrrol bromide reacts with ethyl formate to produce the required aldehyde,¹⁹ and the same substance is obtained by the action of *iso*amyl formate on pyrrole in presence of sodium.²⁰ In this connexion, it is interesting to note that Angeli and Alessandri²¹ have put forward the view that the compound in question is not a true aldehyde, but has the hydroxymethylenic structure:



The synthesis of a new colouring matter from pyrrole²² seems likely to yield materials for further investigations, for the new substance is allied on the one hand to the triphenylmethane dyes and on the other to difluorene, fulvene, indigotin, and possibly to hæmin and chlorophyll as well. The reaction between benzophenone and pyrrole (in alcoholic solution with a trace of hydrochloric acid present as a catalyst) yields two main products, namely, diphenyl-2-pyrrolylcarbinol and diphenyldi-2-pyrrolylmethane. The latter is derived from the former by the interaction of a second molecule of pyrrole. It appears that the carbinol can be prepared also by the action of magnesium pyrrol bromide on benzophenone, and the removal of the elements of water from it results in the formation of a colouring matter which has the following structure:



Treatment with zinc dust and hydrochloric acid converts the coloured base into the corresponding leuco-compound,



The colouring matter dyes tissues raspberry-red, and the tints appear to be stable.

Pyridine.

In the Report of last year²³ attention was called to the use of pyridine as a solvent and catalytic reagent, and during the present twelvemonth there has been a further addition to our knowledge in this branch of the subject.²⁴ When thiophenol is dissolved in

¹⁹ V. V. Tschelincev and A. Terentéev, *Ber.*, 1914, **47**, 2652; *A.*, i, 452.

²⁰ L. Alessandri, *Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 65; *A.*, i, 452.

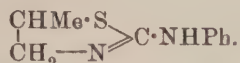
²¹ A. Angeli and L. Alessandri, *ibid.*, ii, 93; *A.*, i, 454.

²² V. V. Tschelincev, B. V. Tronov, and A. P. Terentéev, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1211; *A.*, i, 990.

²³ *Ann. Report*, 1914, 146.

²⁴ M. Raffo and G. Rossi, *Gazzetta*, 1915, **45**, i, 28; *A.*, i, 86.

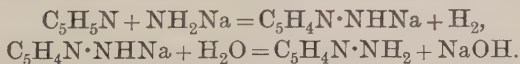
pyridine, the solution, on boiling, yields phenyl disulphide as a principal product. The evolution of hydrogen sulphide indicates that other reactions also take place in the solution. A pyridine solution of thiobenzanilide also liberates hydrogen sulphide when it is boiled, and if the heating is continued until no further evolution of gas takes place, the principal product is a substance which may be either $\text{NPh}\cdot\text{CPh}\cdot\text{NPh}\cdot\text{CSPh}$ or $\text{NPh}\cdot\text{CPh}\cdot\text{S}\cdot\text{CPh}\cdot\text{NPh}$. Similar treatment converts phenylallylthiocarbamide into hydrogen sulphide, allylthiocarbamide, and *N*-phenylpropylene- ψ -thiocarbamide:



An examination of some selenium compounds shows that they also are decomposed by heated pyridine. Diphenylseleniocarbamide yields hydrogen selenide and carbodiphenylimide; but further reactions then occur which end in the production of aniline, triphenylguanidine, and carbanilide.

Pyridine is acted on by sodium at the ordinary temperature, and when the reaction is carried out in an atmosphere of nitrogen the product is obtained quite pure.²⁵ No gas is evolved, and in the final substance it is found that pyridine is present in the proportion of two molecules of pyridine to one atom of sodium. When the experiment is carried out with the reagents in other proportions there is always a residue of the substance present in greatest quantity. The compound $(\text{C}_5\text{H}_5\text{N})_2\text{Na}$ thus obtained seems to be analogous to the ammonia derivative $(\text{NH}_3)_5\text{Na}$. Picoline behaves in the same manner as pyridine so far as this reaction is concerned.

Another new reaction of the pyridine nucleus²⁶ appears to be capable of wider extension. Sodamide is allowed to react with pyridine and the temperature is maintained below 120° . When the reaction has run its course, the product is decomposed with water, and it is found that a 70 per cent. yield of 2-aminopyridine is obtained. The reactions involved are evidently the following:



Further action of sodamide on pyridine is found to lead to the displacement of both α -hydrogen atoms by amino-radicles, so that 2:6-diaminopyridine is produced. The latter substance seems likely to have a technical importance, since it can be coupled with diazo-compounds, yielding true azo-dyes. Various other compounds have

²⁵ B. Emmert, *Ber.*, 1914, **47**, 2598; *A.*, i, 454.

²⁶ A. E. Tschitschibabin and O. A. Zeide, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1216; *A.*, i, 590.

been obtained by the action of sodamide on pyridine derivatives, but it is unnecessary here to enter into details.

The nitration of pyridine itself presents very considerable difficulties, but the presence of an amino-group in the molecule appears to increase the readiness with which nitration takes place, and it is found that 2-aminopyridine undergoes nitration with almost the same ease as aniline.²⁷ The chief product of the reaction is 5-nitro-2-aminopyridine, although it is accompanied by an isomeric substance which may be 3-nitro-2-aminopyridine. The nitropyridines resemble the nitroanilines to a certain extent, being yellow compounds of feeble basicity. When an attempt is made to diazotise the nitroaminopyridines, no diazo-compound can be isolated; but if the reaction is conducted in concentrated hydrochloric acid solution the amino-group of 5-nitro-2-aminopyridine is replaced by a chlorine atom, so that evidently under these conditions diazotisation does occur.

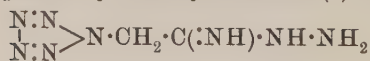
Another amino-derivative of pyridine is obtained by heating 4-chloropyridine with fresh zinc ammonium chloride to 220—230° in a sealed tube.²⁸

Sulphonation of the pyridine nucleus is readily accomplished if the reaction be carried out in the presence of vanadyl sulphate; other catalysts have been examined, but their effect is not so good. Impure pyridine appears to be much less easily sulphonated than the pure substance.²⁹

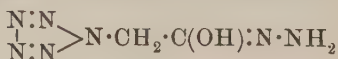
Pentazole Compounds.

Some very interesting compounds containing a five-membered ring built up entirely from nitrogen atoms have been synthesised³⁰ during the current year, and it seems probable that valuable results may follow when the field has been further examined.

If hydrazine hydrate is warmed with an alcoholic solution of cyanotetrazole, ammonia is liberated and a yellow precipitate of pentazolyacetohydrazidine (I) is formed. More ammonia is evolved



(I.)



(II.)

when this substance is boiled with aqueous potassium hydroxide, and the end-product of the reaction is the potassium salt of pentazolyacetohydrazide (II).

Oxidation of this last substance with potassium permanganate in

²⁷ A. E. Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1236; *A.*, i, 591.

²⁸ B. Emmert and W. Dorn, *Ber.*, 1915, **48**, 687; *A.*, i, 584.

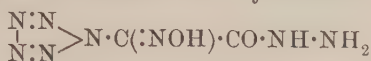
²⁹ H. Meyer and W. Ritter, *Monatsh.*, 1914, **35**, 765; *A.*, i, 715.

³⁰ I. Lifschitz, *Ber.*, 1915, **48**, 419; *A.*, i, 465. [Compare, however, T. Curtius, A. Darapsky, and E. Müller, *ibid.*, 1914, *A.*, 1916, i, 84.]

hot aqueous solution eliminates the hydrazine group with the formation of the potassium salt of pentazolyacetic acid (III). When a suspension of pentazolyacetohydrazine in a solution containing excess of sodium nitrite is treated with hydrochloric acid,

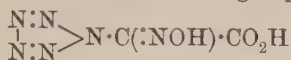


(III.)

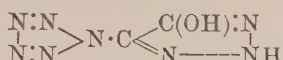


(IV.)

pentazolyloximinoacetohydrazide (IV) separates out in red crystals; this substance readily undergoes change in either of two ways. When heated in alcoholic solution with a little hydrochloric acid it can be hydrolysed to pentazolyloximinoacetic acid (V), whereas if it is allowed to undergo spontaneous condensation it eliminates



(V.)



(VI.)

a molecule of water and forms an unstable triazolone derivative (VI).

Pentazolyloximinoacetic acid is slowly oxidised by an ammoniacal solution of silver nitrate, yielding, apparently, pentazolyglyoxylic acid (VII):



(VII.)

The silver salt of the oximino-acid is soluble in warm potassium hydroxide solution, and when the solution so obtained is treated with silver nitrate and nitric acid a colourless, flocculent precipitate is formed which apparently consists of silver pentazole, N_5Ag .

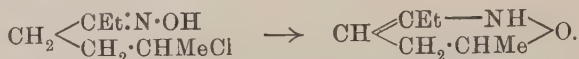
From the foregoing it will be seen that even five-membered nitrogen rings exhibit a marked stability, and further investigations in this field cannot fail to yield results of very considerable value.

The Reactions of the γ -Chloroketones.

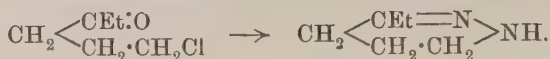
A study of the interactions between various γ -chloroketones and certain amino-derivatives has resulted in the discovery of what appears to be a general method for the preparation of certain heterocyclic substances.³¹ The behaviour of various chloroketones towards ammonia, hydroxylamine, hydrazine hydrate semicarbazide, and phenylhydrazine leads to the following results. Alcoholic ammonia and ethyl γ -chloro-*n*-butyl ketone do not appear to yield any appreciable yield of a base, for the principal product of the reaction is a trimethylenic ketone. The action of hydroxylamine proceeds in two stages, the first of which is oximation, whilst

³¹ H. Wohlgemuth, *Ann. Chim.*, 1914, [ix], 2, 403; *A.*, i, 164.

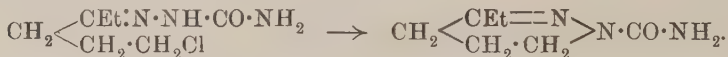
the second produces a cyclic compound. Thus, in the case of ethyl γ -chloro-*n*-butyl ketone, the oxime can be isolated, and when it is heated with pyridine the product is chiefly 6-methyl-3-ethyl-5:6-dihydroisooxazine:



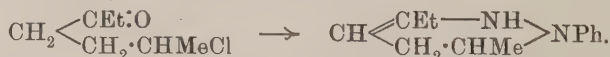
Ethyl γ -chloropropyl ketone reacts analogously, producing 3-ethyl-5:6-dihydroisooxazine. With hydrazine hydrate, the γ -chloro-ketones give rise directly to cyclic compounds. For example, ethyl γ -chloropropyl ketone yields 3-ethyltetrahydropyridazine,



When a concentrated aqueous solution of the hydrochloride of the latter compound is allowed to react with potassium cyanate, the result of the process is to produce 1-carbamyl-3-ethyltetrahydropyridazine. This substance is also obtainable from ethyl γ -chloropropyl ketone and semicarbazide. The semicarbazide is first formed, and on heating in pyridine solution it passes over into the pyridazine derivative, as shown below:



The action of phenylhydrazine on the chloroketones seems to take place in one stage with the production of *N*-phenyltetrahydropyridazines. For instance, in the case of ethyl γ -chloro-*n*-butyl ketone, the end-product of the reaction is 1-phenyl-6-methyl-3-ethyltetrahydropyridazine,



It will be seen that this reaction is capable of wide extension, and may serve to simplify the syntheses of certain heterocyclic substances.

Some Blue Adsorption Compounds of Iodine.

Three years ago, a series of investigations was carried out on the adsorption of iodine by various substances, such as cholalic acid, saponarin, and other natural compounds,³² and this line of work has now been extended to the heterocyclic division of organic chemistry, for it has been observed³³ that numerous synthetic substances of known structure also possess the faculty of forming adsorption compounds with iodine. The newer data are of especial interest, as they open up a line of research which may eventually

³² *J. Barger and Miss E. Field, T., 1912, 101, 1394.*

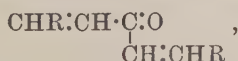
³³ *J. Barger and W. W. Starling, ibid., 1915, 107, 411.*

throw a clear light on the relations between chemical constitution and adsorptive power.

. Blue compounds are not formed by substances in the molecular disperse condition, nor do preformed crystals show absorption phenomena to any noticeable extent. In order to obtain the blue compounds with iodine, it is essential that the adsorbing substance should be present as a colloidal solution or as an amorphous gel. When in the crystalline condition, some of the substances examined gave mixed crystals with iodine, and it was occasionally observed that the blue adsorption compound on keeping became converted into these mixed crystals.

It will be sufficient to mention here the classes of compounds which have been investigated, as it would occupy too much space to deal in detail with the results that have been obtained. About twenty derivatives of α -pyrone were examined, some of which gave mixed crystals, whilst others yielded adsorption compounds. A dozen derivatives of γ -pyrone showed an analogous behaviour. In the case of xanthone and its derivatives no mixed crystals were produced, although adsorption phenomena were observed. In the flavone group, both adsorption and mixed crystal formation were noticed, but it was found that flavanones containing a reduced pyrone ring are indifferent to iodine. The behaviour of pyrone derivatives containing sulphur (such as thiocoumarin, thioxanthone and its allies) was found to be similar to that of the other classes, mixed crystals being observed in some cases, whilst adsorption compounds were formed in other experiments. The thioflavones are similar to the oxygen analogues, except that in the case of the former the adsorption requires longer time to make itself marked.

As regards the influence of chemical structure on the adsorption phenomena, the following facts appear to be important. Taking the case of the pyrone derivatives, it has been found that certain substances give blue compounds, whereas others, very closely allied to them chemically, do not exhibit the phenomena of adsorption to any extent. Thus even a trifling alteration in chemical structure seems to exert a marked inhibitive effect on the process. The presence of a crossed conjugated double linking seems to be of



especial significance in the problem. An increase in the number of the aryl groups in a molecule tends to raise the adsorptive power, whilst the heaping up of alkyl radicles appears to have an opposite effect. On the data available it seems probable that the chief factor in the question is residual affinity, but at present it

is difficult to go beyond this very general statement. Further detailed information will probably lead to most interesting conclusions.

Tetranitromethane as a Reagent for Measuring Residual Affinity.

It has already been pointed out³⁴ that tetranitromethane yields colorations when mixed with compounds containing atoms which are capable of exercising a higher degree of valency, and this work has now been carried further.³⁵ The following heterocyclic substances have been examined: pentamethylene sulphide, 1:4-thioxan, tetrahydro-1:4-thiopyran, and 1:4-dithian. Quantitative investigation with the spectrograph shows that in each case the mixture of tetranitromethane and the compound under examination has selective absorption with a maximum at $1/\lambda$ 2850 and a penetration depending on the time which has elapsed since mixing. This points to the formation of a series of very similar compounds in the mixture, and the increasing penetration of the band is clearly due to the increase in the amount of the product formed as time goes on. Thus the rate of increase in the persistence of the band may be utilised as a test of the velocity of the reaction, and hence as an index of the reactivity of the compound which is reacting with the tetranitromethane. These deductions have been tested in certain cases by comparison with experimental data obtained from actual reactivity measurements, and the agreement between the two sets of results is a close one.

Certain inhibitive factors have been detected in some cases. Thus the presence of a halogen atom in the molecule appears to diminish the reactive power of the compound as compared with that of its halogen-free analogue, and similar results are noted when conjugation occurs within the molecule.

It is pointed out that alkyl nitrites may replace tetranitromethane, and yet the same type of selective absorption is produced, and on this evidence it is assumed that the colorations are not produced by ordinary tetranitromethane, but arise only after the tetranitromethane has undergone intramolecular change into a "nitritic" form. This view is supported by a spectrographic examination of tetranitromethane under various conditions. The influence of the solvent on the reaction has also been studied in some detail.

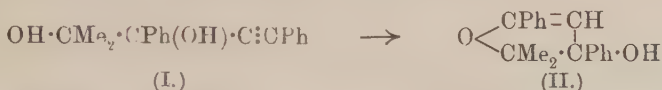
³⁴ H. T. Clarke, A. K. Macbeth, and A. W. Stewart, *P.*, 1913, **29**, 161.

³⁵ E. M. Harper and A. K. Macbeth, *T.*, 1915, **107**, 87; A. K. Macbeth, *ibid.*, 1824.

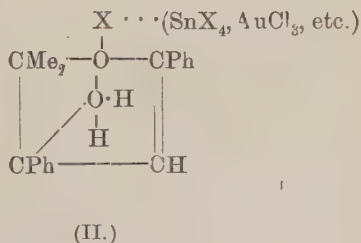
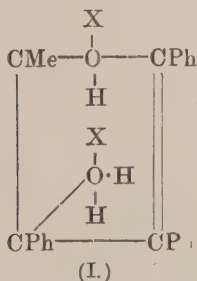
It appears probable that this line of investigation is open to much wider applications, and as it throws a certain amount of new light on the vexed question of intermediate compounds or intermediate "molecular phases" it is to be hoped that further researches will be carried out.

Some Oxonium Compounds.

The interaction of magnesium phenylacetylene bromide and benzoyldimethylcarbinol yields a pinacone (I) which, on boiling with 20 per cent. sulphuric acid, is converted into 4-hydroxy-2:4-diphenyl-5:5-dimethyl-4:5-dihydrofuran (II):



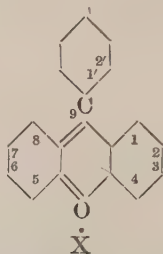
This substance³⁶ appears to have marked basic properties and forms salts which contain two molecules of acid for each molecule of the furan derivative; but it has been noticed that these two molecules of acid are not in a similar condition, since only one of them enters into the constitution of the platinichloride, $(\text{C}_{18}\text{H}_{18}\text{O}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, and similar substances. Since one of the oxygen atoms in the substance is ethereal, whilst the second is hydroxylic, it is assumed that the difference in stability of the two salt groupings has its origin in this factor, and it is supposed that the molecule of acid which is united to the ethereal oxygen is more stable than the other. Thus the salts containing two molecules of acid are regarded as having the constitution I, whilst those containing one molecule of acid have had the structure II ascribed to them. In the platinichloride and analogous compounds, the extra atoms are supposed to be attached to the group X by auxiliary valencies.



A study of the influence of substituents on the stability of

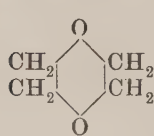
³⁶ A. Favorski and Mlle. E. Venus, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 133; *A.*, i, 289.

oxonium salts of 9-phenylxanthonium has been carried out with the following results: ³⁷

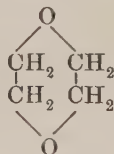


The unsubstituted salts exist only in the solid state or in presence of a large excess of a strong acid; the introduction of methyl groups in the positions 2 and 7 has little influence, but the substitution of methyl for hydrogen in the positions 3 and 6 apparently increases the stability of the salts to at least a hundred times the original value. The presence of a carboxyl group at the position 2' lowers the stability markedly, but the esterification of the carboxyl group tends to raise the stability of the oxonium derivatives again.

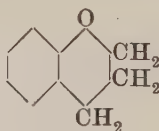
A somewhat more extensive series of investigations in the same direction has been commenced, of which the first part has been published.³⁸ The substances chosen for examination belong to six-membered cyclic systems of the following types:



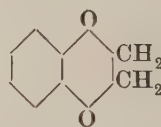
(I.)



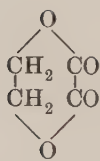
(II.)



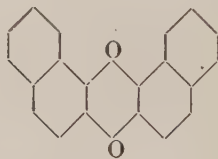
(III.)



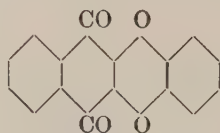
(IV.)



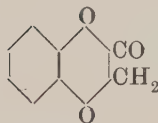
(V.)



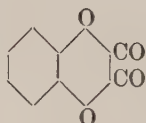
(VI.)



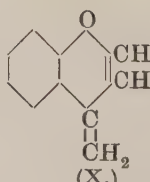
(VII.)



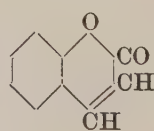
(VIII.)



(IX.)



(X.)



(XI.)

³⁷ F. Kehrman and A. Bohn, *Ber.*, 1914, **47**, 3052; *A.*, i, 575.

³⁸ B. N. Ghosh, *T.*, 1915, **107**, 1588.

In order to study the basic properties of these oxygen derivatives, perchloric acid has been selected, and with this reagent the following results have been observed.

When one oxygen atom alone is a member of the ring, the power of salt-formation is much influenced by the nature of the remainder of the molecule. Thus tetrahydropyran (I) and dihydrobenzpyran (III) yield no salts, but the presence of further unsaturated radicles seems to enhance the basicity of the oxygen atom, since salts are formed by 1-methylene-1:4-benzopyran (X), the coumarins, and the γ -pyrone derivatives. Somewhat similar phenomena are observed in the case where the six-membered ring is built up partly from two oxygen atoms. Dioxan (II) and benz-dioxan (IV) yield no perchlorates, but the power of addition is gained when extra unsaturation is found in the molecular structure, as in the case of diketodioxan (V), di- $\alpha\beta$ -naphthdioxin (VI), diketobenz- $\beta\beta$ -naphthdioxin (VII), ketodihydrobenzdioxin (VIII), and diketodihydrobenzdioxin (IX), all of which yield perchlorates.

From these results it seems fair to deduce that the power of bivalent oxygen to form additive compounds with acids is increased by the entrance into the molecule of "negative" radicles such as the ethylenic bond or the carbonyl group.

Further investigations on the nature of dimethylpyrone hydrochloride have been made,³⁹ and from evidence based on conductivity measurements it is concluded that the substance is a true salt which is correctly represented by the oxonium formula. In this connexion it may be well to mention that a study of certain amino-derivatives of camphoric acid⁴⁰ leads to the conclusion that cyclic salts are formed having the structure $R\text{--}\overset{\text{CO}}{\underset{\text{NH}_3}{\text{C}}}\text{--}\text{O}$, so that the views of Werner on the nature of "onium" salts receive no support in this region.

Pyrones and their Allies.

An attempt⁴¹ has been made to obtain reduction products of dimethylpyrone by means of various agents. As was already known, zinc dust and glacial acetic acid do not effect this reduction, but the addition of concentrated hydrochloric acid produces a bluish-violet coloration. When magnesium powder is substituted for zinc dust, the process seems to be facilitated. The reduction product

³⁹ H. N. K. Rördam, *J. Amer. Chem. Soc.*, 1915, **37**, 557; *A.*, i, 292; compare *Ann. Report*, 1914, 130, and A. Baeyer and J. Piccard, *Annalen*, 1915, **407**, 332; *A.*, i, 290.

⁴⁰ W. A. Noyes and R. S. Potter, *ibid.*, 189; *A.*, i, 79.

⁴¹ A. Baeyer and J. Piccard, *Annalen*, 1915, **407**, 332; *A.*, i, 290.

has not been isolated, but its perchlorate appears to have the composition $C_{14}H_{16}O_2 \cdot HClO_4$. The reduction of dimethylpyrone by magnesium powder, glacial acetic acid, and methyl alcohol in the absence of air produces a leuco-compound of the colour base mentioned above. This leuco-compound seems to have the formula $C_{14}H_{18}O_2$, and shows no reaction with alkalis, ammonia, potassium, cold benzoyl chloride, or phenylhydrazine. In acetone solution it is oxidised by air when an aqueous mineral acid is present. A glacial acetic solution of the leuco-compound in an atmosphere of carbon dioxide takes up two atoms of bromine and is converted into a derivative of the colour-base. Two further atomic proportions of bromine can react with this last substance, giving a dehydro-derivative.

Another, and apparently cleaner, method of reduction which can be employed in the pyrone series is the action of hydrogen in the presence of palladium and gum arabic. In this way 4-pyrone is reduced to the tetrahydro-derivative, whilst dimethylpyrone and ethyl chelidonate yield analogous products. It has been observed that the reduced compounds boil at much lower temperatures than do the parent substances.

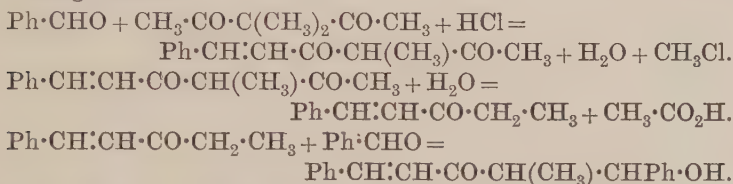
A study of the condensation of aldehydes with β -diketones⁴³ has led to the syntheses by this method of certain reduced pyrone derivatives, and as the results appear to demonstrate the errors of a previous experimenter,⁴⁴ they may be given here in some detail. The action of benzaldehyde on acetylacetone in the presence of alcoholic hydrogen chloride does not produce the expected condensation product $CHPh \cdot CH \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$, but yields a substance containing chlorine which, when heated in a vacuum, forms an oily compound having the structure $CH_3 \cdot CO \cdot C(:CHPh) \cdot CO \cdot CH_3$. The reaction can be made to take another course by introducing two methyl radicles in place of hydrogen atoms in the methylene group of the acetylacetone. When this is done the condensation with benzaldehyde yields bright red crystals which when exposed to air eliminate hydrochloric acid and become colourless. The colourless substance has the composition $C_{25}H_{23}O_2Cl$, and when heated with pyridine it produces a crystalline substance of the composition $C_{25}H_{22}O_2$. The latter compound reacts with hydroxylamine and with bromine; additive compounds are formed in each case between one molecule of the compound and one molecule of hydroxylamine or bromine. Prolonged boiling with alkali has no effect on the colourless substance, which is therefore not a β -diketone derivative of the normal type. The reaction with hydroxylamine points to

⁴² W. Borsche, *Ber.*, 1915, 48, 682; *A.*, i, 574.

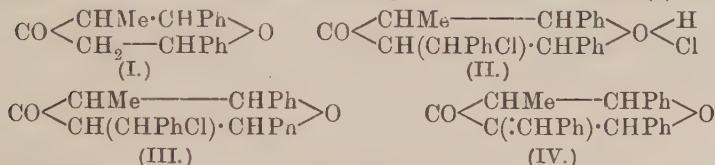
⁴³ H. Ryan and J. M. Dunlea, *ibid.*, 1914, 47, 2423; *A.*, i, 416.

⁴⁴ M. G. Heller, *ibid.*, 887, 2998; *A.*, 1914, 563, 417.

the presence of the grouping $\cdot\text{C}:\text{C}\cdot\text{CO}\cdot$ in the molecule, whilst the formation of an unstable red additive compound with hydrochloric acid indicates that the substance contains a pyrone nucleus. The substitution of methylacetylacetone for the dimethyl derivative makes no alteration in the end-product of the reaction, whence it follows that one or more methyl radicles evidently are eliminated during the operations. This and other evidence leads to the conclusion that the series of reactions can best be formulated in the following manner:

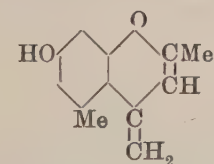


The latter compound is then changed into an isomeride (I) which

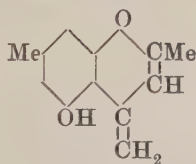


reacts with benzaldehyde and hydrochloric acid to form the unstable red oxonium salt (II). Hydrochloric acid is then eliminated, with the result that (III) and (IV) are produced in succession.

Following upon previous studies of the reactions shown by substances containing one or more "keten" groups,⁴⁵ a further advance has been made in the current year.⁴⁶ It has already been shown that diacetylacetone can be converted, by loss of the elements of water, into either dimethylpyrone or orcinol, and it has now been found that when the latter compound is condensed with acetylacetone, which also contains the "keten" group, two new basic substances are produced, which belong to the benzopyranol series, and are therefore allied to natural dyes, such as apigenin. The two substances have the structures shown below:



Gives lemon-yellow hydrochloride.

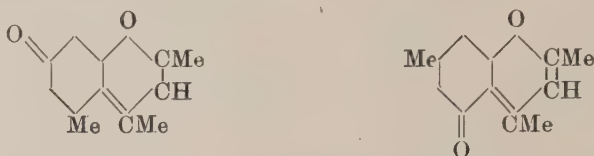


Gives orange hydrochloride.

⁴⁵ J. N. Collie, *T.*, 1907, **91**, 1806.

⁴⁶ J. N. Collie and G. N. White, *ibid.*, 1915, **107**, 369.

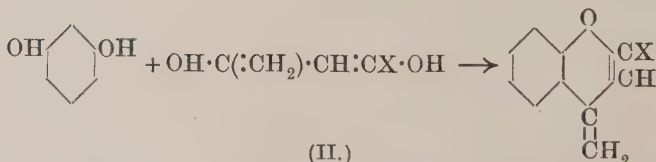
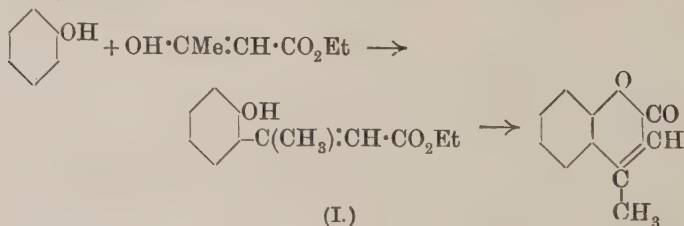
It is possible to write the structure of these compounds in the quinonoid form thus:



but it should be noted that attempts to prove the presence of a carbonyl radicle have failed in each case, whereas acetylation of the hydroxyl group appears to be relatively simple. The acetyl derivatives seem to have lost the power of salt-formation which is possessed by the parent substances. The following explanation appears to cover most of the facts. In the free state or in the form of salts both substances are quinonoid; when the acetyl derivative is formed no quinonoid structure can be produced, so that the compound is colourless. In sodium hydroxide solution, which favours the production of the hydroxyl form, the substances are weakened in colour, in one case becoming almost colourless.

Benzopyrone and Flavone Derivatives.

When ethyl acetoacetate is condensed with phenols in the presence of sulphuric acid the reaction produces coumarin derivatives, as shown in (I); whereas the interaction of a *m*-dihydroxyphenol and acetyl- or benzoyl-acetone in the presence of hydrogen chloride results in the formation of methylene-substituted pyrones as in (II):

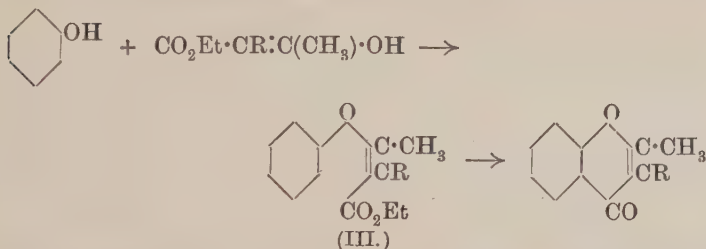


The corresponding reaction has now been studied⁴⁷ with ethyl acetoacetate, in which the active hydrogen atoms have been replaced by alkyl groups. In the case of the dimethyl derivative

⁴⁷ S. Jacobson and B. N. Ghosh, *T.*, 1915, **107**, 424, 959, 1051.

of ethyl acetoacetate no condensation occurred at all. The mono-ethyl derivative yielded a mixture of two substances which were supposed to be a γ -benzopyrone and a coumarin; whilst when ethyl benzylacetoacetate was used, the product was found to be a γ -benzopyrone. These results establish the fact that the complexity of the substituent group has a very marked influence on the course of the reaction.

It is possible to assume that when there is no substituent present the reactivity of the hydrogen atom is very great, and that the hydroxyl group of the ester condenses at once with the hydrogen atom in the ortho-position with respect to the hydroxyl group of the phenol, whilst in the second stage of the reaction a molecule of alcohol is eliminated, as is shown in (I). On the other hand, when a monomethyl-substituted ester is employed, the reactivity of the remaining hydrogen atom in the methylene group is diminished by the substitution, and it is unable to condense with the hydrogen atom attached to the benzene nucleus. It has still sufficient reactivity left to enable it to condense with the phenolic hydroxyl group, and the reaction ends with the elimination of ethyl alcohol and ring-formation as shown in (III). A very



considerable amount of data has been accumulated with regard to the influence of substituents on the reaction, but it is impossible to deal with the matter fully in a Report.

A richly hydroxylated flavone derivative⁴⁸ has been prepared by condensing 2:4:6-trimethoxyacetophenone with the trimethyl ether of methyl gallate in the presence of sodium, and demethylating the product by boiling it with hydriodic acid. Under this treatment the initially formed hexahydroxybenzoylacetophenone loses the elements of water and yields 5:7:3':4':5'-pentahydroxyflavone. Attempts were made to reduce this substance by the action of hydrogen and palladium-black under low pressure, but no results were obtained.

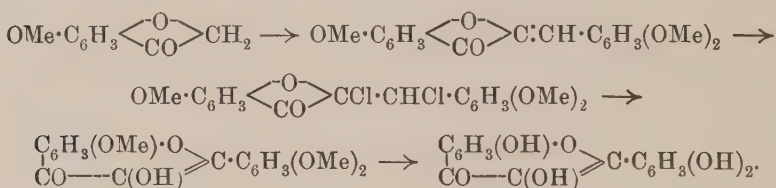
In continuation of the work begun last year⁴⁹ further attempts

⁴⁸ G. Bargellini and L. Monti, *Gazzetta*, 1915, **45**, i, 64; *A.*, i, 84.

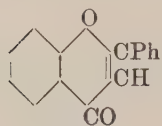
⁴⁹ *Ann. Report*, 1914, 133.

have been made⁵⁰ with the object of deepening the colour of flavone derivatives by the introduction into their nuclei of auxochrome groups. Luteolin and morin ethers have been nitrated, and the nitro-groups have been reduced to amino-groups. The influence of the new auxochromes has been studied spectroscopically, and it has been found that a multiplication of auxochrome groups results in a widening of the principal absorption band and a slight shift in its position towards the red end of the spectrum. The effect on the second band which lies in the violet and ultra-violet is apparent in the spectroscope; but so far as visible appearances go the alteration in this band has little influence on the colour of the substances.

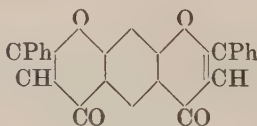
A new synthesis of fisetin⁵¹ has been devised which is based on the following scheme of reactions. The yield obtained is, however, only 5 per cent. of the theoretical in the case of fisetin trimethyl ether, and a further loss will naturally occur before fisetin itself can be liberated:



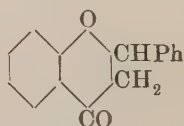
An entirely new type of flavone derivative has been obtained this year⁵² which may become of considerable technical importance. It may be well to illustrate its relation to the ordinary members of the flavone series by formulæ:



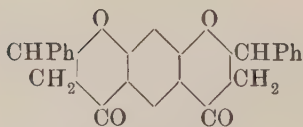
Flavone.



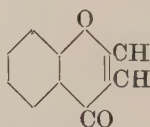
Diflavone.



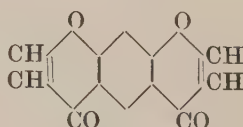
Flavanone.



Diflavanone.



Chromone.



Dichromone.

The new substance has been termed diflavone, and the names

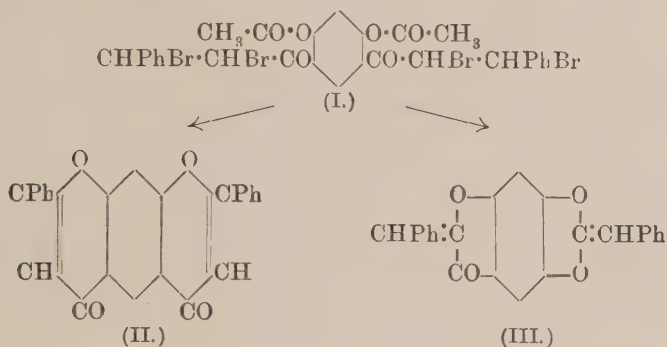
⁵⁰ A. G. Perkin and E. R. Watson, *T.*, 1915, **107**, 198.

⁵¹ K. von Auwers and P. Pohl, *Ber.*, 1915, **48**, 85; *A.*, i, 154.

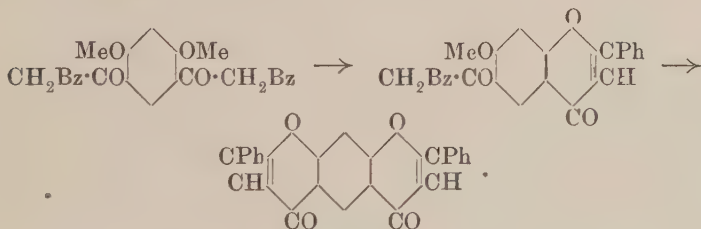
⁵² H. Ryan and Miss P. O'Neill, *Proc. Roy. Irish Acad.*, 1915, **32**, 48, 167; *A.*, i, 707, 1071.

dichromone and diflavanone have provisionally been attached to the still unknown but corresponding substances.

Diflavone is obtained as follows: Dimethyldiacetoresorcinol when allowed to react with benzaldehyde produces the dimethyl ether of dihydroxydichalkone, from which by acetylation and bromination the diacetate of dihydroxydichalkone tetrabromide was synthesised. The latter compound (I) when acted on by alcoholic potassium hydroxide, produces a mixture of diflavone (II) and dibenzylidenedicoumarinone (III):



Another method of synthesis starts with dibenzoylaceto-resorcinol dimethyl ether, which, on boiling with concentrated hydriodic acid, is converted in two successive stages into benzoylaceto-methoxy-flavone, and finally diflavone:



Owing to the fact that diflavone contains no auxochrome groups it is not to be expected that it would be strongly tinted, and its actual colour is a very faint yellow, scarcely differing from ordinary colourless flavone. The effect of auxochromes on the molecule is at present under examination.

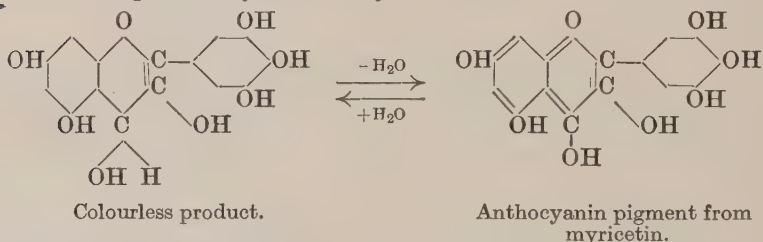
Plant Pigments and Allied Materials.

In this field of investigation our knowledge is becoming very much more extensive than seemed likely a few months ago. At present the methods of research are chiefly being directed to acquiring a general knowledge of many of the plant pigments rather

than a detailed acquaintance with single derivatives, but none the less a considerable amount of information with regard to particular compounds is being acquired.

Certain yellow flavonol derivatives have been submitted to gentle reduction,⁵³ and the substances resulting from this operation have been compared with natural cyanin. Resemblances can be traced between the natural and artificial compounds in the following respects: (1) Stability in acid solution; (2) absorption spectrum, consisting of a single broad band, which becomes flatter towards the violet and extends over a great part of the green and blue regions; (3) oxidation in acid solution with the production of colourless products; (4) loss of colour on reduction, with restoration of the colour on addition of hydrogen peroxide; (5) formation in neutral solution of violet or reddish-violet compounds, giving red oxonium salts with acids and blue or bluish-green compounds with alkalis; (6) instability in presence of alkalis; (7) decolorisation in neutral solutions (due to isomerisation) and quantitative return of the colour on adding acid.

This is explained by Everest by the scheme:



and this explanation is supported by evidence from other workers.

Some investigations of rutin have led to the discovery of a red anthocyanin which may prove identical with cyanin, but the proof of identity is not yet complete.

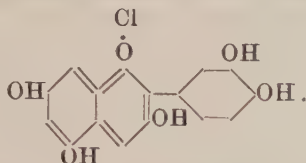
The colouring matter of the rose has been investigated,⁵⁴ and it has been shown that the anthocyanin present in this plant is identical with that previously discovered in the cornflower. This fact is established by an examination of the absorption spectra, specific rotations, solubilities in ethyl alcohol, and dilute hydrochloric acid of the cyanin chlorides, and it is further supported by the hydrolysis of the substances to cyanidin and dextrose (2 mol.), which has been carried out quantitatively.

The formula of cyanidin chloride has been modified by further investigation. The substance has been found to retain one molecule

⁵³ A. E. Everest, *Proc. Roy. Soc.*, 1914, [B], **88**, 326; *A.*, i, 25; compare *Ann. Report*, 1914, 140.

⁵⁴ R. Willstätter and T. J. Nolan, *Annalen*, 1915, **408**, 1; *A.*, i, 282.

of water with great tenacity, and this had been included in the early formula for the substance. The actual composition of cyanidin chloride is therefore $C_{15}H_{11}O_6Cl$, and not $C_{16}H_{13}O_7Cl$. This new formulation of cyanidin is of importance,⁵⁵ since it brings into one natural family pelargonidin, cyanidin, and delphinidin, which differ from each other in the number of hydroxyl groups that they contain. It seems probable that cyanidin chloride has the following structure, whilst pelargonidin chloride contains one hydroxyl group less (that in the 3'-position), and delphinidin chloride contains an extra hydroxyl radicle in the 5'-position:



The colouring matter of the whortleberry (*Vaccinium vitis idaea*) has been isolated and has received the name idæin.⁵⁶ It is closely allied to cyanin. On hydrolysis, it yields galactose (1 mol.) and cyanidin, which is identical with the cyanidin obtained from the cyanin of the rose and cornflower.

The flowers of scarlet pelargonium (*Pelargonium zonale*, var. *meteor*) have now been found⁵⁷ to contain only a single colouring material, which is termed pelargonin. It forms scarlet oxonium salts, and occurs in this form in the flowers. On hydrolysis it yields dextrose (2 mols.) and pelargonidin.

Further investigations in this field⁵⁸ have been concerned with the colouring of the hollyhock (*Althaea rosea*), which is due to althæin; of the wild mallow (*Malva silvestris*), the anthocyanin of which has been named malvin; and of the peony, which is produced by peonin.

Controversy has arisen⁵⁹ with regard to the results obtained in the past with regard to the colouring matters of the grape and of the bilberry. From the results now at our disposal, Willstätter and Zollinger suggest that myrtillidin chloride (from bilberries) and ænidin chloride (from grapes) are respectively the 7-monomethyl and the 3:4'-dimethyl ethers of delphinidin chloride.

The anthocyanin delphinin occurs in the flowers of the larkspur (*Delphinium consolida*), and has been extracted from them by a

⁵⁵ R. Willstätter and H. Mallison, *Annalen*, 1915, **408**, 15; *A.*, i, 282.

⁵⁶ R. Willstätter and H. Mallison, *ibid.*, 15; *A.*, i, 282.

⁵⁷ R. Willstätter and E. K. Bolton, *ibid.*, 42; *A.*, i, 283.

⁵⁸ R. Willstätter and K. Martin, *ibid.*, 110; R. Willstätter and W. Mieg, *ibid.*, 122; R. Willstätter and T. J. Nolan, *ibid.*, 136; *A.*, i, 287-8.

⁵⁹ R. Willstätter and E. H. Zollinger, *ibid.*, 83; *A.*, i, 285.

simple method.⁶⁰ When hydrolysed with hot hydrochloric acid, delphinin chloride is converted into dextrose (2 mols.), *p*-hydroxybenzoic acid (2 mols.), and delphinidin chloride, $C_{15}H_{11}O_7Cl$, the constitution of which was mentioned above. Delphinidin chloride is a quinonoid oxonium salt which forms blue salts with alkalis and red salts with acids, whilst in neutral solution it passes into the ψ -base.

This investigation has been of exceptional interest from the theoretical point of view for the following reason: Delphinin differs from other anthocyanins which have hitherto been examined in one important respect. When it is dissolved in neutral solvents it remains stable and is not converted into a ψ -base, and since it is insoluble in water and also in concentrated alcohol it can be isolated without the use of chemical reagents. When this is done it is found that the substance occurs in flowers unaccompanied by any mineral constituent. Now in earlier papers Willstätter and his collaborators advanced the theory that the varied colours of many flowers were produced by a single anthocyanin, which, acting as an indicator, exhibits a red, violet, or blue colour according as the cell-juice of the plant in that particular case is acid, neutral, or alkaline. The isolation and examination of the colouring material has confirmed this view. The violet colouring matter is neutral. The addition of alkali alters the colour to blue, whilst the acidification of the substance changes its tint to red. This subject is dealt with in more detail in a further paper.⁶¹

The Alkaloids.

In former years the main lines of research in this field pointed in the direction of the determination of the constitutions of certain better-known but still unsynthesised alkaloids; in the period at present under review, however, this trend has been less marked, and, instead, the attention of chemists seems to be mainly directed towards the isolation of new natural substances and to the tentative experiments which mark the first steps in our knowledge of such compounds. It will be convenient to deal chiefly with the commoner alkaloids in the first place, and after this some of the newly discovered compounds will be discussed.

It may be recalled that there is a general agreement with regard to the probable formula for cinchonine, although the exact position of a methylene group has not been determined with absolute certainty; and in any of the recognised structures for the alkaloid there are two points at which a reducing agent might make its

⁶⁰ R. Willstätter and W. Mieg, *Annalen*, 1915, **408**, 61; *A.*, i, 284.

⁶¹ R. Willstätter and H. Mallison *ibid.*, 147; *A.*, i, 289.

attack. These two points are the vinyl group and the pyridine nucleus. It has been shown⁶² that the application of Tafel's electrolytic method yields a product containing four extra hydrogen atoms, but a re-examination of the products has led to results somewhat more complicated than were originally described. Instead of a single reduction product, a mixture of two bases was obtained, the one of which is crystalline, whilst the other is oily. Both have the composition $C_{19}H_{24}N_2$. The nature of the crystalline base appears to be placed beyond doubt by the fact that oxidation converts it into deoxycinchonine, from which evidence it seems safe to assume that the base itself is dihydrodeoxycinchonine. When it is reduced by means of sodium and amyl alcohol it is converted into a viscous oil which is apparently tetrahydrodeoxycinchonine.

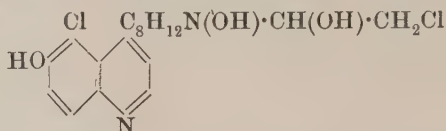
The fact that during the reduction of the dihydro- to the tetrahydro-compound two extra hydrogen atoms have attached themselves to the partly reduced pyridine nucleus and have not disturbed the vinyl group appears to be supported by the following evidence. Paal's method of reduction when applied to cinchonine produces cinchotine by an attack on the vinyl radicle; it might be expected that similar results would be obtained in the case of dihydrodeoxycinchonine. When this compound is reduced in aqueous alcoholic solution in the presence of hydrogen and colloidal platinum, however, it does not yield the tetrahydrodeoxycinchonine, but an isomeride, which, from analogy, should be dihydrodeoxycinchonine. In this substance it seems reasonable to assume that the vinyl group has been reduced, as was the case in cinchonine itself, so that the isomeric compound obtained by the reduction with sodium and amyl alcohol is probably a tetrahydropyridine derivative which contains the vinyl group intact.

The action of chlorine on quinine and some of its derivatives has been very fully studied.⁶³ The method employed was to dissolve quinine hydrochloride in hydrochloric acid and then treat it with one, two, or three molecular equivalents of chlorine. When the alkaloid and chlorine interact in equimolecular proportions an additive product, quinine dichloride, $C_{20}H_{24}O_2N_2Cl_2$, is formed, which behaves as a diacidic base, the derivatives of which resemble the corresponding derivatives of quinine. Energetic treatment with alcoholic potassium hydroxide eliminates two molecules of hydrogen chloride from the base and produces dehydroquinine. The action of two molecules of chlorine on a single molecule of

⁶² M. Freund and J. A. W. Bredenberg, *Annalen*, 1914, **407**, 43; *A.*, **i**, 159.

⁶³ A. Christensen, *Ber. Deut. pharm. Ges.*, 1915, **25**, 256; *A.*, **i**, 711.

quinine hydrochloride produces the dihydrochloride of a base which is supposed to have the following formula:

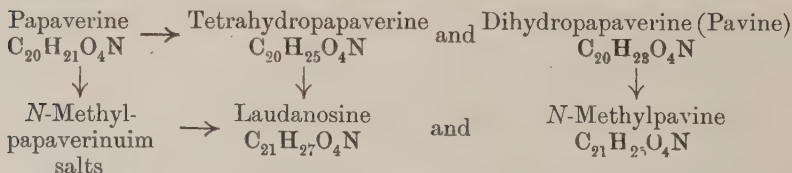


When three molecular proportions of chlorine act on quinine hydrochloride an unstable base is produced having the composition $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}_2\text{Cl}_3$; and a similar base containing one atom less oxygen is formed by the action of chlorine on hydrochloroquinone. The difference between the two substances is ascribed to the displacement of the hydroxyl group by hydrogen in the side-chain of the first substance. Both bases liberate iodine from potassium iodide, so it seems probable that each contains the grouping $\cdot\text{CO}\cdot\text{CCl}_2$ in the quinoline nucleus.

When quinine dichloride is allowed to react with two further molecular proportions of chlorine, it does not yield the base produced by the direct action of three molecular equivalents of chlorine on quinine hydrochloride, but instead a new compound is formed having the composition $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_2\text{Cl}_4$. This has been found to contain only one active chlorine atom, displaceable by the action of potassium iodide.

Reference may be made to some work on strychnine and brucine,⁶⁴ and also to the establishment of the fact that oxalic acid and an amino-acid of the composition $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_2$ occur as fission products⁶⁵ of strychninolonic acid- α .

Before entering into the recent work on the constitution of pavine⁶⁶ it may be well to indicate briefly the relations between the alkaloids of this family so that the general bearing of the investigation may be appreciated. The following scheme will suffice:



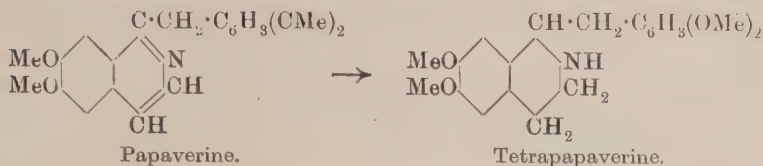
With regard to the formation of tetrahydropapaverine from papaverine and of laudanosine from N-methylpapaverinium salts, the

⁶⁴ R. Ciusa and L. Vecchiotti, *Atti R. Accad. Lincei*, 1914, [v], **23**, ii, 480; *A*, i, 893.

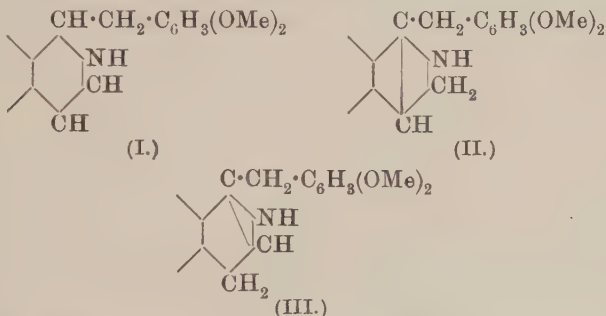
⁶⁵ H. Leuchs and G. Schwaebel, *Ber.*, 1915, **48**, 1009; *A.*, i, 713.

⁶⁶ F. L. Pyman, *T.*, 1915, **107**, 176.

reaction depends on the reduction of the *isoquinoline* to a tetrahydro*isoquinoline* nucleus, as is shown in the following formulæ:



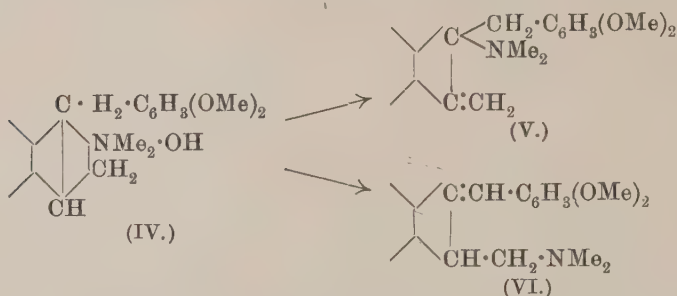
The operation which results in the formation of pavine from papaverine is not so clear. Pavine is a secondary base, so that one of the two new hydrogen atoms certainly has attached itself to the nitrogen atom. This leaves the second hydrogen atom still unaccounted for, and it might be supposed to attach itself at either the 1-, 3-, or 4-position. Pavine might thus be supposed to have one of the three structures represented below:



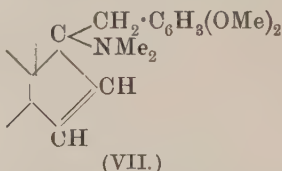
It is well established that 1:2-dihydro*isoquinoline* derivatives are readily susceptible to oxidation and reduction; pavine, on the contrary, is stable towards oxidising and reducing agents, so that on this ground it is possible to exclude the first formula from consideration. This leaves a choice between II and III. Now when Hofmann's degradation method was applied to *N*-methylpavine methohydroxide, $\text{C}_{22}\text{H}_{28}\text{O}_4\text{N} \cdot \text{OH}$, the first product on boiling with concentrated aqueous potassium hydroxide was found to be the corresponding methine, $\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}$, and oxidation of this substance with aqueous potassium permanganate produced a dicarboxylic acid, $\text{C}_{22}\text{H}_{27}\text{O}_8\text{N}$, a reaction which points to the presence of the group $\cdot\text{CH}:\text{CH}\cdot$ in the methine. Further, since there has been no loss of carbon atoms during the oxidation, it is clear that the unsaturated grouping is not essential to the coherence of the molecule.

These facts cannot be brought into accordance with formula II, for if pavine had a structure of this type, *N*-methylpavine methohydroxide would have the formula IV and might form either of

the methines represented by V and VI, neither of which could yield a dibasic acid on oxidation without the loss of carbon:



Pavine must therefore have the structure represented in III, and its methine can be represented by VII, which would readily yield the required dicarboxylic acid:



Further evidence in support of this view is obtained from the behaviour of the methine methiodide towards water and methyl alcohol, whereby trimethylamine hydriodide is readily eliminated, a reaction which tends to show that the grouping $\cdot\text{NMe}_3\text{I}$ is attached to the carbon atom of a negative group—in this case the benzene nucleus.

The synthesis of alkaloid derivatives of high molecular weight⁶⁷ has been studied in the condensation of papaverine with formaldehyde and with opianic acid in the presence of sulphuric acid. Opianylpapaverine and methylenedipapaverine have thus been produced, but the only point of interest in the work appears to lie in the fact that the methylenedipapaverine thus formed differs from that obtained when no sulphuric acid is present.⁶⁸

In the hydrastine group very little work of interest has been done during the present year. A new synthesis of hydrastinine derivatives⁶⁹ by the condensation of homopiperonylamine compounds of the type $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CHAlk} \cdot \text{NR} \cdot \text{CHO}$ (where R=hydrogen, alkyl, or arylalkyl) has been patented, and a some-

⁶⁷ M. Freund and K. Fleischer, *Ber.*, 1915, **48**, 406; *A.*, i, 449.

⁶⁸ W. Königs, *ibid.*, 1899, **32**, 3599; *A.*, 1900, i, 189.

⁶⁹ E. Merck, D.R.-P. 279194; *A.*, i, 709.

what analogous method⁷⁰ has been applied to the preparation of hydrohydrastinine and its homologues.

In the morphine group, the main progress of the year has been made in the increase of our knowledge of the action of acetic anhydride on the morphine derivatives.⁷¹ It has been shown that the morphine series can be separated into three classes according to the effects of the action of acetic anhydride on the various members. Morphothebaine, *apocodeine*, *apomorphine* and its derivatives behave, in the presence of acetic anhydride, in a manner analogous to the tertiary benzylamines; fission of the molecules occurs at the nitrogen atoms. A double fission at the nitrogen atom and also at a carbon atom takes place in the case of thebaine, codeinone, and ψ -codeinone. The members of the third class of compounds, which comprises codeine, morphine, thebainone, and phenyldihydrothebaine, undergo no change in structure.

Tiffeneau suggests that the action of acetic anhydride takes place in two successive stages in those cases where fission occurs; the first step is the addition of the anhydride to the tervalent nitrogen atom, whilst the subsequent fission is to be attributed to the instability of the grouping containing quinquevalent nitrogen. This view is supported by the fact that when polarimetric readings of thebaine in the presence of acetic anhydride are taken, there is a marked falling off in the *lævorotation* during the first twenty-four hours. At this stage, treatment with water regenerates the original alkaloid from the additive product, but if the reaction is allowed to proceed further, fission occurs.

A very careful examination of the reactions of dihydroberberine⁷² has been made, but neither the experimental work nor even the arguments deduced from the results can be summarised here without occupying much more space than could be spared. Those who are interested must therefore read the eighty-page paper for themselves.

The current year has been marked by the closer investigation of certain of the less known members of the alkaloid group, and although the results in most cases have not sufficed to throw a definite light on the constitutions of these substances, none the less they seem worthy of mention here. That interesting substance, yohimbine (or quebrachine), has been subjected to a most careful examination, with the following results.⁷³ It appears to

⁷⁰ E. Merck, D.R.-P. 280502; *A.*, i, 710.

⁷¹ M. Tiffeneau, *Bull. Soc. chim.*, 1915, [iv], 17, 67, 109; M. Tiffeneau and Porcher, *ibid.*, 114; *A.*, i, 448-9; compare also M. Freund and E. Speyer, *Ber.*, 1915, 48, 497; *A.*, i, 560.

⁷² M. Freund and K. Fleischer, *Annalen*, 1915, 409, 188; *A.*, i, 982.

⁷³ G. Barger and Miss E. Field, *T.*, 1915, 107, 1025.

have the composition $C_{22}H_{28}O_3N_2$ and contains one methoxy-group. It is a monacidic tertiary base and forms a methiodide which crystallises with one molecule of water. When brominated in chloroform solution, it combines with a molecule of bromine without any evolution of hydrogen bromide, producing the hydrobromide of monobromoyohimbine, whilst further bromination of this substance yields the hydrobromide of dibromoyohimbine. Both bromo-derivatives, like the methiodide, contain a molecule of water more than the base itself. Yohimbine, when treated with concentrated sulphuric acid, yields a sulphonic acid, and this fact, taken in conjunction with the results of bromination, appears to point to the presence of one benzene ring in the yohimbine molecule. The possibility of a second benzene ring being present appears to be excluded by the high hydrogen content of the base. Oxidation of yohimbine has not led to any very marked advance in our knowledge, although various reagents were tried. Degradation of the alkaloid by means of soda-lime led to the isolation of a substance which appears to be an indole derivative, and another compound which seems to contain a pyridine ring associated with a benzene nucleus.

The problem of aconitine⁷⁴ has again been attacked in the last twelvemonth, but the results do not carry us much beyond what was already known, although a new method of oxidation has been devised which produces oxonitin in yields much higher than have hitherto been obtained. The older method consisted in decomposing aconitine permanganate with sulphuric acid, but it now appears that considerable loss occurs owing to the hydrolysis of the permanganate by the sulphuric acid employed in the reaction. When the method is modified by using permanganate in acetone solution and employing glacial acetic acid, the reaction gives a 90 per cent. yield of oxonitin.

Further investigations of the angostura alkaloids have been carried out, the nature of *isocusparine* being the object in view,⁷⁵ but the results do not lend themselves to summarisation here.

The degradation of colchicine⁷⁶ has been investigated, with the following results. When oxidised with hot potassium permanganate solution, the alkaloid yields a trimethoxy-*o*-phthalic acid the nature of which is determined from the fact that it produces gallic acid when it is boiled with hydriodic acid. The action of nitric acid on colchicine produces a mixture of succinic, oxalic,

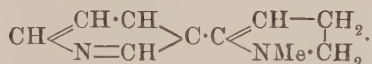
⁷⁴ G. Barger and E. Field, *T.*, 1915, **107**, 231.

⁷⁵ J. Tröger and W. Müller, *Arch. Pharm.*, 1914, **252**, 459; *A.*, i, 459.

⁷⁶ A. Windaus and L. Krellwitz, *Sitzungsber. Heidelberg. Akad. Wiss. Math. Naturw. Klasse.*, [A], 1914, 18; *A.*, i, 708.

and picric acids, whilst the two aliphatic acids are obtained from colchicine acid by treatment with potassium permanganate. Fusion with potassium hydroxide and subsequent oxidation with hot potassium permanganate converts colchicine into terephthalic and trimellitic acids, and the same compounds are obtainable from colchicine acid by simple fusion with alkali. This tends to show that colchicine contains a pyrogallol ring and, in addition, a second ring which yields terephthalic and trimellitic acids on fusion with alkali. The action of iodine on an alkaline solution of colchicine results in simultaneous substitution and oxidation, with the results expressed in the following equation: $C_{21}H_{23}O_6N + 4HI + 5NaOH = C_{20}H_{22}O_5NI + 3NaI + Na_2CO_3 + 3H_2O$. The new substance does not give the ferric chloride reaction of colchicine, nor is this reaction observed even after the iodine atom has been removed from the nucleus.

The study of the alkaloids contained in Turkish tobacco has led to definite results.⁷⁷ Four substances have been isolated: nicotine, isonicotine, nicotone, $C_8H_{11}N$, and nicotelline. *iso*Nicotine, $C_{10}H_{12}N_2$, shows reactions which point to its having the following structure:



The pareira root alkaloids have been examined,⁷⁸ but the results do not seem suitable for condensed description. Eserine, derived from the Calabar bean, has been studied and several of its derivatives have been prepared.⁷⁹ A new alkaloid of the bean, geneserine,^{79a} has been isolated, and its reactions have been carefully examined. Another new member of the alkaloid class, struxine, has been discovered in samples of *nux vomica* which had been subjected to the ravages of insects and had become partly decomposed owing to prolonged exposure on wet fields.⁸⁰ It is supposed to be a decomposition product of strychnine or of brucine under the conditions of fermentation or oxidation which had prevailed in the previous history of the beans in which it was discovered. Sempervirine, a third alkaloid from gelsemium, has been isolated and examined; but the results are merely in the preliminary stage, and reference must be made to the original paper

⁷⁷ E. Noga, *Chem. Zentr.*, 1915, i, 434; *A.*, i, 711.

⁷⁸ M. Scholtz and O. Koch, *Arch. Pharm.*, 1914, 252, 513; *A.*, i, 450.

⁷⁹ M. Polonovski, *Bull. Soc., Chim.*, 1915, [iv], 17, 235; *A.*, i, 891.

^{79a} M. Polonovski and C. Nitzberg, *Bull. Soc. Chim.*, 1915, [iv], 17, 244, 290; *A.*, i, 892, 987.

⁸⁰ H. H. Schaefer, *Pharm. J.*, 1915, 94, 241; *A.*, i, 86.

for fuller information.⁸¹ Channa,⁸² described as "a delicacy of the Hottentots," has been found to owe its interest to the alkaloid mesembrine, $C_{16}H_{19}O_4N$, the action of which is said to resemble that of cocaine, although it is distinct from that drug.

Chlorophyll.

In last year's Report the decline in interest with regard to chlorophyll was noticeable, and during the current year very little fresh information has been acquired in this field. A summary of our knowledge on this and allied topics is to be found in a paper by Willstätter,⁸³ but as the matter has been very fully dealt with during previous years, it seems unnecessary to go over the ground again in this place.

The fluorescence of different varieties of chlorophyll has again been examined,⁸⁴ and the results in the main concord with what had already been published on the subject. The chlorophyll of green plants is apparently composed of two fluorescent substances, (*a*) having a band at λ 68—65·5, whilst (*b*) has a band at λ 65·8—65·3. On the other hand, the chlorophyll derived from *Phaeophyceae*, *Diatomaceae*, and *Hydrurus* is quite different. In the living state it shows only one band (that of *a*), whilst when dead it gives a second band, at 64·0—63·0, which is quite distinct from that of *b*, and apparently may correspond with the chlorophyll constituent *c*, the existence of which seems to be in doubt.

A physiological theory of the action of chlorophyll has been put forward by Ivanovski,⁸⁵ and this author considers in turn the influence which the different pigments of plants exert during the vital processes. The original paper should be consulted for the details.

More purely chemical is another investigation,⁸⁶ in which the various pigments occurring in the green leaf have been separated and the action of light on each of them has been studied. It is found that when chlorophyll, xanthophyll, and carotin are exposed to light in presence of excess of oxygen, they may act as oxydases, not only to themselves, but also to other substances, such as litmus, hydriodic acid, or guaiacum. It is therefore unnecessary to assume

⁸¹ A. E. Stevenson and L. E. Sayre, *Pharm. J.*, 1915, **94**, 159; *A.*, i, 85.

⁸² C. Hartwich and E. Zwicky, *Apoth.-Zeit.*, 1914, **29**, 925, 937, 949, 961; *A.*, i, 710.

⁸³ R. Willstätter, *Ber.*, 1914, **47**, 2831; *A.*, i, 289.

⁸⁴ A. Wilschke, *Zeitsch. wiss. Mikroskop.*, 1915, **31**, 338; *A.*, i, 829.

⁸⁵ D. Ivanovski, *Ber. Deut. bot. Ges.*, 1914, **32**, 433; *A.*, i, 705.

⁸⁶ A. J. Ewart, *Proc. Roy. Soc.*, 1915, [B], **89**, 1; *A.*, i, 706.

that peroxides are formed during the photo-oxidation of these pigments. Chlorophyll and xanthophyll decompose during photo-oxidation into formaldehyde and certain waxy solids which contain optically active hexoses. The results vary according as the atmosphere is moist or not. In dry air free from carbon dioxide the reaction tends to produce relatively more formaldehyde and less sugar, whilst the reverse is found when moisture is present. Carotin oxidises more rapidly than either chlorophyll or xanthophyll, and the end-products in its case are a small amount of formaldehyde and much colourless, waxy, solid material.

Chlorophyll combines with carbon dioxide, with the formation of xanthophyll and a waxy solid. This reaction takes place vigorously in sunlight when water is present. Oxygen is evolved, and this in sunlight may oxidise the xanthophyll to formaldehyde, sugar, and the phytol radicle, from which chlorophyll may again be built up.

Xanthophyll can readily be converted into carotin by the action of magnesium powder or zinc dust in water; the reaction proceeds in the dark.

These results show that the assimilation of carbon dioxide by the plant is a very complex process. Chlorophyll and xanthophyll both play their part in the reactions; the equilibrium between the products and the reacting substances determines the direction of the reaction, and light has a strong influence.

One of the most suggestive researches on the chlorophyll problem has resulted in the synthesis of a pigment which appears to present many of the properties shown by natural chlorophyll.⁸⁷ The matter is so important that a detailed description of the results seems justified. Chlorophyll might be regarded as a product formed by the oxidation and polymerisation of aniline according to the equation



Now, when nitrous acid is added drop by drop to a very concentrated solution of aniline in alcohol, a white deposit is formed which turns rose-coloured. Heat is then developed, energetic effervescence takes place, and the deposit becomes green. At the end of the reaction the walls of the vessel are found to be coated with a green or reddish-brown substance, and a dark residue is found at the bottom. By shaking with benzene, a green, fluorescent solution is formed, which becomes red on exposure to air and light. A brown precipitate forms which has the properties of Pringsheim's hypochlorin. If the benzene solution is evaporated

⁸⁷ Albert and A. Mary, *Mon. Sci.*, 1915, [v], 5, 121; *A.*, i, 979.

in the dark, dichroic crystals are formed, which are said to be synthetic chlorophyll.

The reaction may be altered by the addition of sodium hydrogen carbonate to the solution when it becomes green. All the colouring matter can then be extracted by means of benzene, but the solution under certain conditions has the colour of dead leaves. It is claimed that the colour changes which chlorophyll undergoes in nature can thus be artificially brought about in the course of a few minutes. Similar colour reactions can be produced with natural chlorophyll.

It must be frankly admitted that if these results prove to be accurate, they will revolutionise the whole of our views on chlorophyll and will invalidate all the work which has been done in recent years; for, since no magnesium is present in the reacting substances, no magnesium atom can be essential to the production of chlorophyll, and consequently the whole of Willstätter's conclusions would go by the board at a stroke. It is as yet too early to pronounce definitely on the question, but further results will be awaited with considerable anxiety.

The Bile and Blood Pigments and their Allies.

The chemistry of the bile pigments has of recent years become one of the most perplexing and confusing of all the subjects included in the present section of the Annual Reports, and it seems almost too much to hope that we are approaching a solution of the difficulties which confront investigators in this branch of the subject. Data which appear to be fairly based on accurate experiment turn out next year to be erroneous, and the final stage of things seems to be even worse confounded than the crude beginnings. To add to the difficulties of the Reporter, the various investigators delight in acute controversy, and polemical papers abound. During the past year the work in this division of chemistry has consisted for the most part of scattered researches which cannot be welded into a consecutive narrative, so that it seems best in this place to give short summaries of the various investigations without attempting to follow the matter into any great detail.

Bilirubin,⁸⁸ mesobilirubin, and mesobilirubinogen⁸⁹ have been submitted to further examination, and some new reactions have been recorded. The authors have prefaced their papers by a summary of their previous work so as to assist the reader. Certain phenomena point to the possibility that bilirubin is a mixture of

⁸⁸ W. Küster, *Zeitsch. physiol. Chem.*, 1915, **94**, 136; *A.*, i, 829.

⁸⁹ H. Fischer, *Zeitsch. Biol.*, 1914, **65**, 163; *A.*, i, 148.

two modifications, and that a solvent may disturb the equilibrium between the two. The substance now termed mesobilirubinogen is what used to be called hemibilirubin. This continual shifting of nomenclature is by no means the least of the troubles which beset those who wish to read up the subject. When heated with a 10 per cent. solution of potassium methoxide at 150° , mesobilirubinogen is converted into mesobilirubin, but if the temperature is raised to 170° the reaction takes a different course and xanthobilirubic acid is also formed. A further rise in temperature to 190° results in a better yield of the acid. Mesobilirubin can be converted into mesobilirubinogen by the action of sodium amalgam, but biological methods do not seem capable of producing this change.

Some work has been done on the constituents of gall-stones.⁹⁰

A paper on hæmatoporphyrin⁹¹ is largely taken up with controversial matter, and definite data bearing on the crucial points at issue are not available. Arguments are adduced against Willstätter's views, and certain experimental evidence is brought forward with the idea of disproving his conclusions. The controversy appears to centre about the existence of auxiliary valencies in the hæmin group, and as there appears to be considerable doubt as to whether or not such things exist at all, it seems best to leave the matter until better evidence is obtainable.

Another speculative paper⁹² containing a summary of previous work on the subject has been published on hæmopyrrole. It also treats of the possible constitution of hæmin. The extraordinary difficulty of work in this branch of the subject is well exemplified by the fact that a substance originally called phyllopyrrole, and then rechristened hæmopyrrole-*d*, is now found to contain a second compound, which has received the name hæmopyrrole-*g*, and is probably 2:3-dimethyl-4:5-diethylpyrrole. Phonopyrrolecarboxylic acid-*a* can be converted into the picrate of hæmopyrrole-*b*, and since the constitution of the latter is known, it is possible to deduce the structure of phonopyrrolecarboxylic acid-*a*, which is apparently



Now, since the oximes of phonopyrrolecarboxylic acid-*b* and phonopyrrolecarboxylic acid-*a* are isomeric, and both give the same hæmatic acid, it follows that phonopyrrolecarboxylic acid-*b* (sometimes called *isophonopyrrolecarboxylic acid*) must be 2:5-dimethyl-

⁹⁰ W. Küster, *Zeitsch. physiol. Chem.*, 1915, **94**, 163; *A.*, i, 831.

⁹¹ W. Küster and H. Bauer, *ibid.*, 172; *A.*, i, 853.

⁹² O. Piloty, J. Stock, and E. Dormann, *Annalen*, 1914, **406**, 342; *A.*, i, 451.

pyrrole-4- β -propionic acid. Since phonopyrrolecarboxylic acid-*c* (also called xanthopyrrolecarboxylic acid) gives the same oxime and the same hæmatic acid as phonopyrrolecarboxylic acid-*b*, it is assumed that it is probably 3-methyl-5-ethylpyrrole-4- β -propionic acid. Phonopyrrolecarboxylic acid-*d* is supposed to be 2:3:5-trimethylpyrrole-4- β -propionic acid. These four acids are obtained by the action of hydrogen iodide on hæmin in glacial acetic acid.⁹³

In the same paper it is pointed out that hæmopyrrole-*e* cannot be 2:3-dimethyl-1-ethylpyrrole, because a pyrrole derivative of this structure has now been synthesised, and it is found that its picrate differs from that of hæmopyrrole-*e*.

Another polemical paper⁹⁴ contains, in addition to controversial material, an account of certain experiments on the condensation of glyoxal with members of the pyrrole series, whilst still another contribution⁹⁵ is largely taken up with a claim for priority, although it also describes the formation of some dipyrromethane derivatives by the interaction between pyrrole compounds, chloroform, and alkali.

Annual Reports are by their very nature somewhat lacking in coherence, but in former years the Reporter has been able to comfort himself with the idea that he has at least drawn attention to one or two outstanding lines of research and has sketched their progress in its broad outlines. In the foregoing Report he is only too conscious that such sections are conspicuous by their absence. The study of the heterocyclic compounds during the last twelve months has not produced any researches which in themselves can be termed epoch-making, and with the best will in the world one cannot make bricks without straw. It would, however, be a mistake to suppose that this indicates a failure of research in the field at the present time. Annual Reports are only a by-product of chemical investigation, and the fact that a Report is somewhat dry should not suggest that the subject is bankrupt. In the case of the present year, much useful knowledge has been added to our stock, and if the researches of the past twelve months have not presented anything of a spectacular nature they have laid a very sound foundation for work in the future.

A. W. STEWART.

⁹³ It seems desirable to note that the formation of the oximes referred to above is not a direct reaction, since none of the acids contains a ketonic carbonyl radicle.

⁹⁴ H. Fischer, *Ber.*, 1914, **47**, 3266; *A.*, i, 309.

⁹⁵ O. Piloty, W. Krannich, and H. Will, *ibid.*, 2531; *A.*, i, 461.

ANALYTICAL CHEMISTRY.

COMPARED with other years, 1915 saw scarcely any diminution in the number of papers relating to analytical chemistry, but, as might be expected, many well known names will be absent from this year's index, their owners being engaged on work of more immediate importance than analytical research. Of the papers published, a much smaller proportion than usual are suitable for mention in this Report, which will, in consequence, be short compared with those of other years.

Physical Analysis.

The incidence of cathode rays on certain salts produces immediately vivid colours on the salts, which in the dark and at low temperatures may persist in some cases for many years. Thus sodium chloride becomes amber-coloured, potassium chloride violet, potassium bromide deep blue, sodium fluoride rose, lithium chloride bright yellow, and potassium carbonate red. The colours are sensitive to heat in very different degrees; for instance, that of sodium chloride is comparatively stable, but those of potassium chloride and bromide disappear even at tropical temperatures. The disappearance of colour in daylight is generally accompanied by the appearance of marked fluorescence. Similarly, solid solutions of these salts even in extreme dilution, in substances such as potassium or sodium sulphate, which are not themselves affected by cathode rays, also acquire characteristic colours, generally different from the colour given by the pure substance. Thus, one part of potassium carbonate in 25,000 parts or more of the sulphate produces a green colour, whilst in some cases quantities of an admixture estimated at one part in one million, may produce a perceptible tint. These reactions afford a very sensitive method for detecting impurities in salts, even when more than one impurity is present, since the colours produced by different impurities generally disappear at different rates in daylight or on increasing the temperature. Potassium sulphate, for example, generally turns dark grey at first, owing to the presence of a trace of sodium chloride, but this

colour disappears in a short time in daylight, leaving only a vivid green due to the carbonate. Since the colorations produced by different salts of the same metal vary so much, it is probable that they are due primarily to the acidic group. This assumption is strengthened by the fact that the halogen derivatives of acetic acid are coloured by the cathode rays, whilst acetic acid itself remains colourless. These phenomena are probably accounted for by a decomposition, not, however, of the ordinary kind in which the components are entirely set free, but merely a "distention," the components remaining at a short distance from one another, and, if the absorptive power is weakened by heating, or the chemical affinity strengthened by the energy of daylight, recombination again ensues. The effects of cathode rays and β -rays are really the effects of the ultra-violet light produced by the stopping of those rays, and hence ultra-violet light also produces similar colour effects on salts.¹

Using a fluorescence microscope, nearly a hundred different substances have been examined in ultra-violet light, and more than a third of them are found to fluoresce. It is suggested that the fluorescence of arsenic trioxide, sodium uranyl acetate, sodium pyrantimoniate, silver and mercurous haloids may prove useful in qualitative analysis.²

Only a single paper need be cited in connexion with the use of the interferometer for the analysis of solutions. In this paper the remarkable claim is made that a mixture of potassium and sodium sulphates can be analysed by this means with an accuracy even greater than that attainable by the most careful gravimetric work.³ The ease and rapidity of the method were long since demonstrated.

A new method for the estimation of acidity has been based on the observation that the addition of a strong capillary-inactive acid (a strong acid which, on dissolving in water, does not lower the surface tension of the solvent) to the capillary-inactive salt of a weaker capillary-active acid sets the weak capillary-active acid free and causes a lowering of surface tension, from which the quantity of strong acid added can be calculated.⁴ Alkalis are similarly estimated by the lowering of the surface tension of solutions of the salts of alkaloids with strong acids.⁵

The method for the determination of hydroxyl-ion concentration,⁶ based on the velocity of hydrolysis of nitrosotriacetoneamine, has

¹ E. Goldstein, *Rep. Brit. Assoc.*, 1914, *Chem. News*, 1915, **111**, 27.

² W. Lenz, *Zeitsch. anal. Chem.*, 1915, **45**, 27; *A.*, ii, 275.

³ L. H. Adams, *J. Amer. Chem. Soc.*, 1915, **37**, 1181; *A.*, ii, 478.

⁴ I. Traube and R. Somogyi, *Inter. Zeitsch. Phys.-chem. Biol.*, 1914, **i**, 479; *A.*, ii, 101.

⁵ I. Traube, *Ber.*, 1915 **48**, 947; *A.*, ii, 571.

⁶ *Ann. Report*, 1913, 162.

been so modified that its accuracy has been much increased with but slight increase in the time necessary to complete a determination. A serious defect of the nitrosotriacetoneamine method was the fact that between concentrations of $0.05N$ and $0.3N$ the unimolecular constants "drifted," and the method was consequently inapplicable within those limits. By the use of nitrosovinylidiacetoneamine or nitrosoisobutyldiacetoneamine, however, it has been found possible to bridge this region of ionic concentration, and the method in one or other of its modifications serves to determine all values of hydroxyl-ion concentration.⁷

Inorganic Analysis.

Qualitative.—A few qualitative tests are deserving of notice. For the detection of white phosphorus in matches a more sensitive and more rapid test than that of Thorpe has been devised. It depends on the volatility of white phosphorus with steam and its luminescence in contact with oxygen, and will detect 0.1 mg. suspended in 10 c.c. of water.⁸ Ilinski and Knorre's reagent for cobalt (α -nitroso- β -naphthol)⁹ has never been much used as it is very unstable, and, in certain circumstances, untrustworthy. It has now been shown that the sodium salt of the oxime is much more stable in solution, and that it will readily detect less than one part of cobalt in one million parts of water. Only large quantities of nickel interfere, and it is easy to precipitate the bulk of the nickel by means of dimethylglyoxime or α -benzildioxime.¹⁰ For many purposes the flame test for sodium is too sensitive. Most other methods are troublesome. A method has recently been described, depending on the separation of potassium perchlorate or borofluoride and detection of sodium by the insolubility of the silicofluoride in alcohol. An advantage of the method is that the previous separation of magnesium, a troublesome operation, is unnecessary. Lithium does not interfere.¹¹

Quantitative.—For the titration of small quantities of haloids Volhard's method is not entirely satisfactory, requiring one drop of $N/10$ -solution to determine the end-point. A method depending on the far more delicate reaction between iodine and starch, using $N/50$ - or $N/100$ -potassium iodide for titrating back the excess of silver, has been found much more satisfactory. The haloid is

⁷ F. E. Francis, F. H. Geake, and J. W. Roche, *T.*, 1915, **107**, 1651.

⁸ E. B. Phelps, *U.S. Hyg. Labor., Bull.* **96**, 51; *A.*, ii, 65.

⁹ *Ber.*, 1885, **18**, 699.

¹⁰ F. W. Atack, *J. Soc. Chem. Ind.*, 1915, **34**, 641; *A.*, ii, 652.

¹¹ F. C. Mathers, C. O. Stewart, H. V. Houseman, and I. E. Lee, *J. Amer. Chem. Soc.*, 1915, **37**, 1915; *A.*, ii, 580.

precipitated in the presence of a known amount of free nitric acid with excess of *N*/50-silver nitrate, the precipitate is coagulated by shaking with a few drops of octyl alcohol, the mixture filtered, and the filtrate mixed with a mixed reagent containing sodium nitrite to liberate iodine, starch, and a sodium salt of a weak acid in amount equivalent to the nitric acid present. The mixture is then titrated with *N*/50- or *N*/100-potassium iodide.¹²

As the result of a critical examination of the most generally approved methods for the analysis of hypochlorite solutions, Bunsen's original method, namely, delivery of the bleach liquor into an excess of potassium iodide solution, addition of acetic acid, and titration of the liberated iodine with thiosulphate, is found to be unapproached in accuracy or in speed by any more recent method. That the method has tended to give way to Penot's method, or to Mohr's more convenient modification of it, is mainly due to the fact that these methods are more economical of iodide and make use of solutions the titre of which remains constant for long periods. The latter characteristic constitutes such a real advantage that Mohr's method of adding excess of arsenite and titrating the excess with standard iodine is likely to remain in use in many laboratories. If it is recognised that the method is empirical and not exact and a suitable correction is applied, results of a very satisfactory degree of accuracy can be obtained.¹³

In the Annual Report for 1912 the attention of agricultural chemists was drawn to Brearley and Ibbotson's lead molybdate method for the estimation of phosphorus,¹⁴ a method long in use in steel works, but one that has become known only slowly to workers in other fields. It is satisfactory to be able to record that the method has now been applied with success to the estimation of minute quantities of phosphorus in physiological material.¹⁵

A new and rapid method for the estimation of nitrates (and nitrites) depends on the fact that they are reduced to ammonia quantitatively and almost instantaneously by titanous hydroxide.¹⁶

A new and rapid, yet accurate, method for the estimation of lead depends on separation as sulphate, decomposition of the sulphate by means of hydrogen sulphide, and titration of the liberated sulphuric acid.¹⁷ It is more accurate than Alexander's

¹² F. C. McLean and D. D. Van Slyke, *J. Amer. Chem. Soc.*, 1915, **37**, 1128; *A.*, ii, 479.

¹³ M. L. Griffin and J. Hedallen, *J. Soc. Chem. Ind.*, 1915, **34**, 530; *A.*, ii, 551.

¹⁴ *Ann. Report*, 1912, 219.

¹⁵ H. S. Roper, *Biochem. J.*, 1914, **8**, 649; *A.*, ii, 66.

¹⁶ E. Knecht, *J. Soc. Chem. Ind.*, 1915, **34**, 126; *A.*, ii, 105.

¹⁷ F. D. Miles, *T.*, 1915, **107**, 988; *A.*, ii, 651.

original molybdate method and quicker than Low's modification of it.¹⁸

Of more importance, perhaps, than any new method for the estimation of copper is a report of the Sub-Committee on Methods of Analysis of Non-Ferrous Alloys of the American Chemical Society. It embodies methods generally accepted in the United States for standard analysis by both producers and consumers of copper and copper products.¹⁹ For the analysis of electrolytic and low resistance copper the method recommended is essentially that of Heath.²⁰ For lower grades of copper special methods are described which circumvent the difficulties introduced by the commoner impurities of commercial copper, whilst keeping the technique as simple as possible. A new modification of the iodine method depends on the action of sodium fluoride on acid solutions of ferric salts, with the iron of which it forms a stable compound, Fe_2F_6 , preventing any subsequent reaction between these salts and potassium iodide. The method is applicable to all kinds of cuprous materials from low-grade ores to regulus, and, although only recently published, has been in daily use for fifteen years, during which its results have been repeatedly checked by refined modifications of the electrolytic method.²¹ According to another new method, cupric solutions are titrated with a standard solution of sodium nitroprusside, the end-point being found by a spotting test with an alkaline sulphide applied to a few drops of the filtered liquid. Neither ferric salts, zinc, alkaline earth metals, manganese, aluminium, tin, nor lead interfere.²² A method for the estimation of cuprous and cupric sulphides in mixtures of both has been based on the fact that cuprous sulphide reacts with silver salts, with the formation of equivalent amounts of metallic silver and silver sulphide, whilst under similar conditions cupric sulphide gives rise only to silver sulphide.²³ For the estimation of copper in steel, a method has been described depending on precipitation as thiocyanate, treatment of the washed precipitate with a measured quantity of potassium iodate solution of known titre, and estimation of the excess of iodate by addition of potassium iodide and titration with thiosulphate. The relation $7\text{KIO}_3 = 6\text{Cu}$ is all that is necessary to calculate the results, but the reactions involved are somewhat intricate, and may be stated as follows:

¹⁸ "Technical Methods of Ore Analysis," 1911, 149.

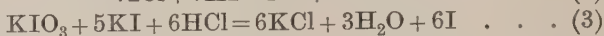
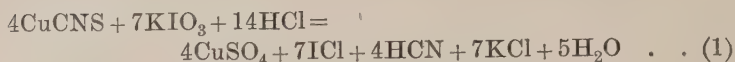
¹⁹ W. B. Price and others, *J. Ind. Eng. Chem.*, 1915, **7**, 546.

²⁰ *Ann. Report*, 1911, 168.

²¹ A. Fraser, *J. Soc. Chem. Ind.*, 1915, **34**, 462; *A.*, ii, 582.

²² G. Zuccari, *Ann. Chim. Applicata*, 1914, **2**, 287; *A.*, ii, 68.

²³ E. Posnjak, *J. Amer. Chem. Soc.*, 1914, **36**, 2475; *A.*, ii, 24,



Equations (1) and (2) show that 7KIO_3 oxidises 4Cu with formation of 7ICl , which, on dilution and treatment with potassium iodide, liberate 14I , or $\text{KIO}_3 = 2\text{I}$, whereas each molecule of iodate in excess of that required by the copper liberates 6 atoms of iodine in accordance with the familiar equation (3). Therefore, one-third of the oxidising power of the potassium iodate taking part in reaction (1) is reclaimed on addition of iodide, and the net consumption of iodate by copper is given by the relation $4\text{Cu} = \frac{2}{3}$ of 7KIO_3 or $6\text{Cu} = 7\text{KIO}_3$.²⁴

A method for the estimation of aluminium in the presence of iron has been based on the fact that aluminium chloride is precipitated completely as the hydrated compound, $\text{Al}_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$, when its concentrated solution is mixed with a solution of 1 part of acetyl chloride in 4 parts of acetone, ferric chloride remaining soluble under these conditions.²⁵ An excellent colorimetric method for the estimation of small quantities of aluminium (0.005 to 0.05 mg. in 10 c.c.) depends on the use of alizarin (red) S, the sodium salt of alizarinmonosulphonic acid. The coloured compound is not a lake, but the aluminium salt of alizarin S. One part of aluminium can be detected in 10 million parts of water, and the method is as nearly quantitative as a colorimetric method can be, even when iron and chromium are present in amounts 1000 times greater than the amount of aluminium.²⁶ The work of Dittrich and his collaborators in reducing the uncertainty of the end-point in the titration of ferrous iron in silicate rocks after decomposition of the rock by means of hydrofluoric acid²⁷ has been carried further by Barnebey, who shows that the most convenient reagent for arresting the tendency of the pink colour to disappear, when the titration with permanganate should be complete, is boric acid, which has the added advantage that ferrous borofluoride is remarkably stable towards atmospheric oxygen (air bubbled through the solution for an hour does not lower its titre), whereas ferrous fluoride is very unstable. Moreover, in the presence of boric acid the customary manganese phosphate solutions may be used to counteract the influence of hydrochloric acid if simultaneously present, whereas in absence of boric acid either manganese salts

²⁴ W. D. Brown, *J. Ind. Eng. Chem.*, 1915, **7**, 213; *A.*, ii, 284.

²⁵ H. D. Minnig, *Amer. J. Sci.*, 1915, [iv], **39**, 197; *A.*, ii, 107.

²⁶ F. W. Atack, *J. Soc. Chem. Ind.*, 1915, **34**, 936; *A.*, ii, 842.

²⁷ *Ann. Report*, 1911, 165.

or phosphates tend to make the end-point very uncertain if hydrofluoric acid is present.²⁸

The accurate analysis of commercial zinc has assumed increased importance with the phenomenal rise in the price of spelter due to the war. No new methods of importance have been described, but a most valuable report has been issued by a Sub-Committee on Methods of Analysis of Non-Ferrous Alloys of the American Chemical Society. The methods recommended are those actually in use in the laboratories of the more important producers and consumers of zinc in the United States. They include an electrolytic method for lead as well as a very accurate, yet simple, modification of the sulphate method, a method for cadmium depending on the separation of pure cadmium sulphide, which is subsequently converted into sulphate and weighed, an alternative electrolytic method for cadmium, and directions for the exact estimation of very small quantities of iron by means of $N/100$ -permanganate.²⁹

In the Annual Report on Analytical Chemistry, 1912, the writer made a very strong claim for the recognition of the perchlorate method, especially the modification of this due to W. A. Davis, as the most accurate method available for the estimation of potassium.³⁰ Thin and Cumming have since cited the writer as sharing the view that the perchlorate method falls short of exactness. It does, like most human efforts, and in 1912 the writer was unwilling to put his case too high, especially as he was publicly castigating a great Department of State for perpetuating the use of the costly, troublesome, and less accurate platinum method. Most of Davis's results published in 1912 were obtained before he effected his final improvement in the method, namely, washing the precipitate with alcohol saturated with potassium perchlorate, but this improvement was fully described in Davis's original paper, and has been followed by Davis and his collaborators at Rothamsted, by the writer, and many others ever since. Thin and Cumming have done good service in showing that this final improvement of Davis reduces the error of the method to less than 0.5 mg.³¹ Perhaps now the Board of Agriculture may begin to consider whether the use of this method for official purposes should be permissive.

The year has witnessed the appearance of a most important paper on the analysis of platinum. Although an unusually good and long abstract appeared in the Journal, no one interested in this

²⁸ O. L. Barnebey, *J. Amer. Chem. Soc.*, 1915, **37**, 1481; *A.*, ii, 583.

²⁹ W. B. Price and others, *J. Ind. Eng. Chem.*, 1915, **7**, 457.

³⁰ *Ann. Report*, 1912, 217.

³¹ R. G. Thin and A. C. Cumming, *T.*, 1915, **107**, 361; *A.*, ii, 281.

subject can do less than study the original paper.³² Fortunately, since German journals are accessible to few just now, the whole paper has been translated and published in English.³³ It deals with the detection and estimation of all the ordinary constituents of commercial platinum in great detail. Fourteen qualitative reactions of each of the six platinum metals in 0.1 per cent. solution are tabulated, the method of carrying out colorimetric estimations with solutions of the chlorides in presence of hydrogen chloride is described, and a simple process for the analysis by precipitation of dissolved platinum alloys is recommended. The behaviour of ruthenium chloride towards ammonium chloride is explained by means of new experiments, and the existence of iridium mercaptide proved. Methods of separating the platinum metals from one another have been tested and improved, and a special method is proposed and described in detail for the quantitative analysis of technical platinum. Finally, for the detection of impurities in high-grade platinum, a method is described as a supplement to that recommended by Finkener, and tested by Mylius and Förster, for the precipitation of the metal.

Few papers have been published this year on the separation of the rare earths. One may be cited. In it experiments are described which show that fractional electrolysis of mixtures of the rare earths yields quite rapid separations in some cases, and that these separations can be effected with far less expenditure of time and labour than by the customary methods of fractional crystallisation or precipitation. The method adopted was the electrolysis of somewhat concentrated, neutral solutions of salts of the rare earths, using a mercury cathode, kept clean by violent agitation with air, and a platinum anode. The most notable result was the complete separation of lanthanum from praseodymium by a very small number (6) of fractional electrolyses. About twice as many operations suffice to separate lanthanum from admixture with praseodymium, neodymium, and samarium, the lanthanum being in each case the last to come out of solution. Yttrium can be almost completely freed from erbium in five operations, but it is much less easy to obtain erbium free from yttrium.³⁴

In the application of Johnson's or similar methods³⁵ for the estimation of vanadium in steel, difficulty is often experienced in producing a colourless or old-rose shade with ferrous sulphate in

³² F. Mylius and A. Mazzucchelli, *Zeitsch. anorg. Chem.*, 1914, **89**, 1; *A.*, ii, 491.

³³ *Chem. News*, 1915, **112**, 88, 104, 125, 134, 144, 155.

³⁴ L. M. Dennis and B. J. Lemon, *J. Amer. Chem. Soc.*, 1915, **37**, 131; *A.*, ii, 99.

³⁵ C. M. Johnson, "Analysis of Special Steels."

the solution containing an excess of permanganate after the preliminary oxidation of the vanadium. A method recently described, depending on oxidation of vanadium with nitric acid, avoids this difficulty. The blank correction is larger than is desirable, but appears to be independent of the weight of the sample, of the presence of chromium, or—within limits—of the carbon content, and the method will estimate proportions of vanadium of the order of 0.2 per cent. with an error not exceeding 0.007 per cent. on the steel.³⁶

The estimation of columbium in presence of tantalum is the subject of a most important paper by Levy, who has investigated a number of methods, and has so far improved on a method devised by Osborne in 1885 that this improved method is likely to be generally adopted, except in cases where time would permit and circumstances might dictate resort to Marignac's original method, which, like all methods depending on fractional crystallisation, is very tedious. Osborne's method³⁷ depended on solution of potassium columbium oxyfluoride in hydrochloric acid, reduction with amalgamated zinc and a piece of platinum foil, and titration with permanganate. It never came into general use, mainly perhaps because Osborne's statement that reduction proceeded as far as a hypothetical oxide, Nb_8O_{13} , rested apparently on a single experiment. Under Levy's modified conditions, reduction only goes as far as $\text{Nb}_{10}\text{H}_{17}$, but under his conditions, which are not at all difficult to attain, reduction does appear to reach and to stop at this point with widely varying quantities of columbium present. Several statements long current and having an important bearing on the estimation of tantalum are shown to be erroneous.³⁸

Organic Analysis.

The usual colour tests for salicylic acid, although extremely delicate, are none of them perfectly characteristic. By combining Kobert's test with Mandelin's, however, a series of colour changes is obtained which is quite distinctive of salicylic acid and salicylates. The reagent is made by mixing equal volumes of 40 per cent. formaldehyde solution and concentrated sulphuric acid and cooling the mixture. A portion of the substance to be tested is moistened in a porcelain dish with this mixture, a little ammonium vanadate is added, and the whole stirred. If salicylic acid is present, a Prussian-blue colour appears immediately, rapidly

³⁶ G. T. Dougherty, *J. Ind. Eng. Chem.*, 1915, 7, 419; *A.*, ii, 490.

³⁷ T. B. Osborne, *Amer. J. Sci.*, 1885, [iii], 30, 329; *A.*, 1886, 393.

³⁸ A. G. Levy, *Analyst*, 1915, 40, 204; *A.*, ii, 491.

changing to greenish-blue, and finally to green. A distinct reaction is given by 0.02 mg. of salicylic acid. A large number of substances, mostly of phenolic constitution, have been tested. Many yield colours, but none can be mistaken for a salicylate.³⁹ A new test has been described which serves to detect 1 part of oxymorphone in 20,000 parts of solution and to distinguish this alkaloid from morphine, codeine, thebaine, apomorphine, quinine, strychnine, brucine, atropine, and caffeine.⁴⁰

For the estimation of bromine and chlorine in organic compounds a method has been based on the fact that organic substances containing these elements give them up entirely in a volatile form when heated with a mixture of chromic acid and sulphuric acid. The final estimation is by titration according to Volhard's method. The results are as accurate as those obtainable by Carius's method, and can be obtained more quickly, with less consumption of the analyst's time, less expense, and no personal risk to the operator.⁴¹ Some useful notes on the Kjeldahl and Dumas methods of estimating nitrogen are included in a paper dealing with the analysis of coal. It is found that coal and probably some other substances must be digested for a considerable time (two hours) after the liquid is colourless if accurate results are to be obtained by Kjeldahl's process. The use of permanganate after the colourless stage is reached shortens the process. It is shown that Dumas's method must always over-estimate nitrogen unless the copper oxide is heated for several hours in a vacuum and cooled in carbon dioxide before using it for a nitrogen determination. Otherwise nitrogen will always be over-estimated and small proportions enormously over-estimated.⁴²

The estimation of toluene in commercial toluol and in commercial solvent naphtha having become of great importance, owing to the demand for the hydrocarbon for the manufacture of trinitrotoluene, two empirical methods for the purpose have been worked out by Colman and Northall-Laurie respectively. Colman's method for commercial toluol consists in distilling 100 c.c. of the sample under prescribed conditions (such that fractionation is reduced to a minimum) and measuring the fraction passing over below 105° and that remaining in the still when a temperature of 117° is reached. By reference to a table the percentage of toluene may then be read off directly if the mixture under examination con-

³⁹ P. A. W. Self, *Pharm. J.*, 1915, **94**, 521; *A.*, ii, 382.

⁴⁰ L. Grimbert and A. Leclère, *J. Pharm. Chim.*, 1914, [vii], **10**, 425; *A.*, ii, 76.

⁴¹ P. W. Robertson, *T.*, 1915, **107**, 902; *A.*, ii, 573.

⁴² A. C. Fieldner and C. A. Taylor, *J. Ind. Eng. Chem.*, 1915, **7**, 106; *A.*, ii, 177.

sists solely of benzene, toluene, and xylene, and contains from 50 to 75 per cent. of toluene. Samples with less than 50 per cent. of toluene are mixed with a known proportion of pure toluene before distillation, whilst high-grade toluols must be diluted with known amounts of benzene and xylene. Correction for paraffins is made by distilling 100 c.c. through a 12-bulb "pear" column and determining the specific gravity of the fraction distilling between 107° and 115°. For every 0.001 that the specific gravity is found below 0.868, a reduction at the rate of $\frac{3}{4}$ per cent. is made on the amount of toluene found by the distillation test and reference to the table constructed for mixtures of pure benzene, toluene, and xylene. Colman fractionates commercial solvent naphtha, collects the fraction distilling below 138°, mixes this with pure toluene and pure benzene in the proportions 7:10:3, and analyses the mixture in the manner above described.⁴³ Northall-Laurie distils 200 c.c. of commercial toluol, collects the first 50 c.c., rejects the next 100 c.c., and then determines the boiling point of the first fraction and of the residue in the still. On reference to a graph prepared as a result of experiments with known mixtures, the percentage of toluene is read off.⁴⁴

Attention was directed in 1912 to Simmonds's modification of Denigès's method for the detection and estimation of methyl alcohol in the presence of ethyl alcohol.⁴⁵ This method has recently been submitted to a critical examination, which showed that close attention to detail was essential if accurate results were to be obtained. The particular details to which attention must be given are now known, however, and if this is given there is no doubt the method is the most accurate yet described, whilst it is among the simplest and quickest.⁴⁶ Thorpe's original method, depending on a different principle, although useful in its day, was very much behind Simmonds's modification of Denigès's method in sensitiveness, and was tending to fall into disuse. Depending as it did on the measurement of the carbon dioxide yielded by the oxidation of methyl alcohol, it had the disadvantage that under Thorpe's conditions ethyl alcohol itself yielded a notable amount of carbon dioxide, and, although this amount could be kept fairly constant, the correction was large, and with small quantities of methyl alcohol present might equal or exceed the amount of carbon dioxide derived from methyl alcohol.⁴⁷ With comparatively little methyl alcohol present, therefore—and this is the most important case in practice

⁴³ H. G. Colman, *J. Gas Lighting*, 1915, **129**, 196, 314; *A.*, ii, 184, 185.

⁴⁴ D. Northall-Laurie, *Analyst*, 1915, **40**, 384; *A.*, ii, 703.

⁴⁵ *Ann. Report*, 1912, 212.

⁴⁶ G. C. Jones, *Analyst*, 1915, **40**, 218; *A.*, ii, 493.

⁴⁷ T. E. Thorpe and J. Holmes, *T.*, 1904, **85**, 1.

—considerable doubt attached to the indications of the method. In this respect the method has been greatly improved by Wilks, who has succeeded in finding conditions of oxidation which reduce the production of carbon dioxide from ethyl alcohol to less than one-fifth of what it might be under Thorpe's conditions. Wilks's conditions of oxidation not only reduce the correction to be applied, but keep that correction much more nearly constant than was the case with Thorpe's method.⁴⁸

The estimation of cellulose and the analysis of cellulose derivatives have been subjects of controversy⁴⁹ so acute that a perusal of the literature by a chemist with no special knowledge of the subject leaves the impression that no existing method can be trusted. In these circumstances a paper by Briggs is of special value. There being no question of the author's knowledge of the literature any more than of his practical experience, it is matter for congratulation that he has not sought to display his erudition, but is content with reference to a few papers and books of outstanding importance. Yet it would be difficult to formulate a question on the estimation of cellulose or the analysis of cellulose derivatives that this paper of Briggs does not answer in terms readily understandable by any chemist, no matter how scanty his previous knowledge of this particular subject.⁵⁰

Reference has been made in earlier Reports to the cryoscopic method for the detection and approximate estimation of added water in milk.⁵¹ Most of the early work was carried out in Australia and Holland, and workers in these countries have again been active,⁵² but it is satisfactory to be able at last to record that the method has been thoroughly investigated in Great Britain. In a report to the Local Government Board, Monier-Williams expresses the opinion that the freezing point appears to be the most constant of any of the properties of milk. Owing, however, to experimental difficulties involved in obtaining trustworthy results, he doubts whether the method is capable of general application for purposes of milk control.⁵³ It has now been shown why the freezing point or osmotic pressure is the most constant factor of pure milk. Genuine but abnormal samples of milk with

⁴⁸ W. A. R. Wilks, *Bull. Wellcome Trop. Res. Lab.*, 1914, **1**, 1; *A.*, ii, 589.

⁴⁹ *Ann. Report*, 1912, 212.

⁵⁰ J. F. Briggs, *Analyst*, 1915, **40**, 107; *A.*, ii, 186.

⁵¹ *Ann. Report*, 1911, 173; 1912, 214; 1913, 183; 1914, 178.

⁵² J. B. Henderson and L. A. Meston, *Proc. Roy. Soc., Queensland*, **24**, 165; *A.*, ii, 28; G. A. Stutterheim, *Pharm. Weekblad.*, 1914, **51**, 1311; *A.*, ii, 29; J. J. van Eck, J. D. Filippo, F. H. van der Laan, A. Lam, A. van Raalte, and L. T. Reicher, *Chem. Weekblad*, 1915, **12**, 108; *A.*, ii, 112; N. Schoorl, *ibid.*, 220; *A.*, ii, 189.

⁵³ G. W. Monier-Williams, *L.G.B. Food Reports*, No. 22, 1914.

unusually low non-fatty solids, but normal freezing point, have been found to be characterised by an abnormally high content of sodium chloride, and there seems no doubt that the mammary glands of the cow, when unable to obtain the correct proportion of milk-sugar and other foodstuffs, adjust the osmotic pressure by adding an extra proportion of sodium chloride from the blood.⁵⁴

In Germany it has been found necessary to devise a special method for the detection of potato starch in bread. This depends on the fact that potato starch takes up certain coal-tar colours much more rapidly than wheat or rye starch. The best colour for the purpose is thionin, but neutral-red or methylene-blue serves.⁵⁵

Among new colour reactions for alkaloids, only one has been sufficiently tested to justify inclusion among these notes. The development of a wine-red colour when heated with sulphuric acid containing 2 per cent. of formaldehyde serves to distinguish cocaine from at least nine other common alkaloids. Papaverine gives a somewhat similar colour, but this changes to yellow, reddish-brown, or orange, whilst the coloration due to cocaine disappears on keeping, leaving a brownish-grey precipitate.⁵⁶

In view of the difficulty introduced into fat analysis by the introduction of hydrogenated products, a newly described colour reaction of marine animal oils, which persists even in artificially hardened fats derived from them, assumes some importance. The reaction depends on the fact that these oils and fats contain a chromogenic substance which reacts with bromine to form a compound that imparts a bright green colour to a chloroform solution of the fat or oil. The test appears to be specific of fats and oils of marine animal origin, and is given by lard substitutes containing as little as 5 per cent. of hydrogenated marine animal oil.⁵⁷ A test which will detect with certainty as little as 5 per cent. of paraffin-wax in beeswax has been based on the fact that when genuine beeswax is saponified with alcoholic potash under definite conditions, the temperature to which the resulting solution can be cooled without the appearance of a cloud is remarkably constant, whereas this temperature is notably raised by small additions of paraffin-wax.⁵⁸

There is still no better agreement as to the best method of estimating caoutchouc in raw rubber than there was when the

⁵⁴ J. B. Henderson and L. A. Meston, *Chem. News*, 1915, **111**, 51.

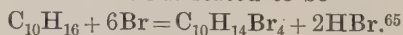
⁵⁵ G. Schütz and L. Wein, *Chem. Zeit.*, 1915, **39**, 143; *A.*, ii, 185.

⁵⁶ F. Pisani, *Rend. Soc. Chim., Ital.*, 1914, **6**, 132; *A.*, ii, 191.

⁵⁷ E. Fortelli and E. Jaffe, *Ann. Chim. Applicata*, 1914, **2**, 80; *A.*, 1914, ii, 822.

⁵⁸ M. S. Salamon and W. M. Seater, *J. Soc., Chem. Ind.*, 1915, **34**, 461; *A.*, ii, 587.

subject was last noticed in these Reports.⁵⁹ The difference method is still the method most used in routine technical analysis, and, within the year, Schidrowitz, in the course of a review of recent advances in the analysis of rubber and rubber goods, has voiced the widely held view that for such work the difference method is the most satisfactory yet available. For research purposes, however, he admits that the direct methods must be kept in view.⁶⁰ Of the older of these methods there is little new to record. As the result of an examination of several methods, Pontio⁶¹ expresses the opinion that the ultimate solution of the problem of estimating caoutchouc directly will be found in some development of Budde's tetrabromide method.⁶² In its present state, however, that method shows no advantage over the best of the simpler solution methods. Of these methods, that of Marquis and Heim^{62a} is condemned by Pontio⁶¹ on the ground that chloroform and other solvents of similarly low boiling point fail to dissolve rubber unless it be quite freshly coagulated or precipitated. If a solvent of higher boiling point, such as xylene, is employed, the solution filtered, concentrated under diminished pressure, and poured into alcohol, results are obtained quite as good as those yielded by any direct method yet described. Results obtained by such a method, if they confirm results obtained by the method of difference, lend added significance to the latter; if they differ, in the present state of our knowledge the results of the difference method should be preferred. Of Alexander's original nitrosite method⁶³ there is nothing new to record, but a modification of it, depending on the determination of the carbon content of the nitrosite precipitate, referred to two years ago, has been further investigated and shown to be fairly trustworthy.⁶⁴ When the analysis of rubber was last considered in these Reports, Vaubel's method was one of a score the history of which had got no farther than the author's original paper. Of the score, it is the only one to have attracted criticism, and this seems to have been met at least as satisfactorily as has the criticism directed against Budde's original method or any of its developments. Vaubel treats a solution of rubber in carbon tetrachloride with potassium bromate, and titrates the excess of the latter in the usual way. The reaction is stated to be



⁵⁹ *Ann. Report*, 1913, 184.

⁶⁰ P. Schidrowitz, *Analyst*, 1914, **40**, 223; *A.*, ii, 496.

⁶¹ Pontio, *Amer. Chim. anal.*, 1914, **19**, 60; *A.*, 1914, ii, 301.

⁶² *Ann. Report*, 1907, 214; 1911, 176; 1913, 184.

^{62a} *Ibid.*, 1913, 184.

⁶³ *Ibid.*, 1907, 214; 1911, 176.

⁶⁴ L. G. Wesson, *J. Ind. Eng. Chem.*, 1914, **6**, 459; *A.*, 1914, ii, 593.

⁶⁵ W. Vaubel, *Gummi-Zeit.*, 1912, **26**, 1879; *A.*, 1913, ii, 630.

It has been alleged that the amount of hydrogen bromide eliminated largely depends on the purity of the reagents, temperature, and concentration.⁶⁶ This criticism seems to have been met satisfactorily, but the author of the method admits that it requires further development before it can be regarded as generally applicable.⁶⁷

Agricultural Analysis.

Several old methods for the estimation of ammonia in soils have been examined and found defective, and a new one believed to be satisfactory has been described. Schlœsing's method fails, because dilute hydrochloric acid does not extract the whole of the ammonia from soils. Of ammonia added as sulphate, not more than 70 per cent. can be recovered. For the same reason Baumann's method, which also depends on extraction with hydrochloric acid, must fail. E. J. Russell's later method,⁶⁸ depending on distillation with very weak alcoholic potassium hydroxide, also fails to return all ammonia added to the soil as sulphate. His earlier method, and all methods depending on distillation with magnesia, lead to the decomposition of organic nitrogenous compounds. The new method is a modification of Folin's method for physiological liquids, the soil being mixed with sodium carbonate solution and the ammonia carried over with standard acid by means of a current of air.⁶⁹ M. Steel's modification⁷⁰ of Folin's method, although apparently an improvement where urine is to be analysed, is quite unsuited to soils. His reagent—weak alkali hydroxide in saturated brine—has the merit of decomposing crystals of magnesium ammonium phosphate, which always separate on adding ammonia to urine, but the concentration of ammonia and water-soluble phosphate in soil is so low that no such crystals are likely to form in the course of soil analysis; and, moreover, Steel's reagent brings about very serious decomposition of the organic, nitrogenous constituents of soil, so that the ammonia in some cases is over-estimated 200 per cent. The view that soils when treated by the new method of Potter and Snyder do not form triple phosphate crystals, with corresponding under-estimation of ammonia, is supported by the fact that seven very different samples gave identical results whether treated by their method or by Folin's modification, in which potassium oxalate is used to prevent the formation of magnesium ammonium phosphate.

⁶⁶ F. Kirchof, *Gummi-Zeit.*, 1913, **27**, 9; *A.*, 1913, ii, 630.

⁶⁷ W. Vaubel and E. Wienerth, *ibid.*, 1913, **28**, 92; *A.*, 1914, ii, 301.

⁶⁸ *J. Agric. Sci.*, 1910, **3**, 233; *A.*, 1910, ii, 1104.

⁶⁹ R. S. Potter and R. S. Snyder, *J. Ind. Eng. Chem.*, 1915, **7**, 221; *A.*, ii, 277.

⁷⁰ *J. Biol. Chem.*, 1910, **8**, 365; *A.*, 1911, ii, 68.

Substances exist in plant material which are soluble in 80 per cent. alcohol, are not precipitated by basic lead acetate, are unfermentable by ordinary yeasts, and reduce Fehling's solution after other sugars present have been fermented. From the fact that the reducing power of such substances, when calculated as a mixture of arabinose and xylose, corresponds with a proportion of pentose nearly identical with that calculated from the Kröber-Tollens phloroglucide distillation, it is assumed that free pentoses are actually present, and that the furfuraldehyde formed on acid distillation does not arise from gums, pentosans, or other sugars present. From the results of nearly 400 fermentation experiments made with extracts of leaves, the amount of the residual reducing power after fermentation with pure cultures of distiller's yeast has been found to be proportional to the pentoses present as estimated by the Kröber method. When only small quantities of other sugars are present, the direct distillation method, with subsequent weighing of the phloroglucide, is quite accurate, but in the presence of large quantities of other sugars these should first be fermented away before applying Kröber's process.⁷¹

The presence of water-soluble compounds of arsenic in arsenical insecticides is objectionable, as such compounds are injurious to foliage, and the laws of the United States set a limit (0.75 per cent. of As_2O_3) to the amount that may be present in arsenate of lead sold for agricultural purposes. As in most cases where a soluble constituent has to be estimated in admixture with a much larger quantity of insoluble material, and especially in the administration of a penal statute, it was necessary to prescribe a particular method of analysis. It has recently been shown that the prescribed method does not extract as much as 70 per cent. of the soluble compounds of arsenic, and a new method has been described yielding results which on the average are 50 per cent. higher than those yielded by the official method. It is also shown that the new method does actually extract soluble compounds, and that the higher results are not due to hydrolysis or other chemical action. The new method consists in macerating the sample (5 grams) with water, transferring the mixture to a filter, and washing it with nearly 1000 c.c. of hot water free from carbon dioxide and ammonia. The soluble arsenate is then estimated in an aliquot portion of the filtrate in any convenient manner.⁷²

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⁷¹ W. A. Davis and G. C. Sawyer, *J. Agric. Soc.*, 1915, **6**, 407; *A.*, ii, 72.

⁷² R. H. Robinson and H. V. Tartar, *J. Ind. Eng. Chem.*, 1915, **7**, 499 *A.*, ii, 581.

PHYSIOLOGICAL CHEMISTRY.

I REMARKED in last year's Report on the growing bulk and importance of the biochemical researches published in the United States. It is not surprising that during the past year the relative prominence of American contributions has still further increased. Papers from the *Journal of Biological Chemistry* will be found indeed to yield a somewhat large proportion of the material dealt with in this Report. Considering the special circumstances of the year, our own output may, it is true, be looked upon as something more than respectable, but very few French, Italian, or Russian papers have been published. The record of German work in the abstracts is incomplete, and I have myself been able to consult but few of the papers in the original.

Animal calorimetry in particular has been developed with great enterprise across the Atlantic, and has reached a degree of accuracy previously unequalled. I am tempted to begin this Report by dealing, in this connexion, with one or two aspects of general metabolism which have received no recent comment.

General Metabolism: the Basal Metabolism of Men and Women: the "Surface Law": the Specific Dynamic Action of Food.

F. G. Benedict has maintained the tradition of his association with Atwater, and has continued, with many co-workers, his admirable calorimetric studies in the Nutrition Laboratory at Boston, where the difficult technique of the subject has been greatly developed under his guidance. G. Lusk¹ has established a small, but accurate, calorimeter in the Cornell University Medical College, which has been successfully used in many experiments on infants and on animals. Owing to Lusk's inspiration and influence, a calorimeter for clinical observations is working under admirable conditions at the Russell Sage Institute of Pathology, which is associated with wards of the Bellevue Hospital, New York.² In this country comparatively little enterprise has been shown on these

¹ *Arch. Int. Med.*, 1915, **15**, 793.

² *Ibid.*, 805.

lines, but we are fortunate in knowing that Macdonald has an efficient instrument, built on the Atwater-Benedict principle, in use at Liverpool.³

Benedict and other American workers have given much attention to what is now known as "basal metabolism," and have determined it on a large number of men and women. This basal metabolism represents the minimal energy exchanges of the body, and is measured when the individual is in a recumbent position and perfectly quiescent. It is determined, moreover, when no digestion or absorption of food is in progress, in what Benedict calls the "post absorptive" period, some fifteen to eighteen hours after a meal. For men weighing near the average of 70 kilos. this basal metabolism is closely equal to one large calorie per kilo. per hour; but any considerable departure from the mean weight involves an appreciable change in the value when it is expressed, as above, in terms of the unit of body-weight.

It is a matter of some importance to decide how nearly we can, by any method of calculation, obtain a definite numerical value for the "normal" metabolism of a given species of animal. When departures from the normal are suspected, observations meant to decide on their magnitude have often to be made on comparatively few individuals; sometimes on one alone. Individuals, however, quite apart from the possession of that particular anomaly or special character which is under study, may differ greatly from the mean in respect of such fundamentals as size and body-weight. How can the effects of such non-significant variations be best eliminated; or, what is the same question in different terms, from what normal base-line can we measure the effect of the significant variations? This is not an academic question; it is of practical importance to physiologists and pathologists, and, no less, to agriculturists concerned with the raising of stock.

In the endeavour to eliminate to some degree the effect of individual variation in size, it has long been customary to express all metabolic data in terms of the unit of body-weight; but it has also long been recognised that values when expressed per kilo. of body-weight do not necessarily become comparable values. Normal metabolism is not simply proportional to body-weight. In the case of human beings Benedict's newer data make this abundantly clear.

Another method commonly supposed to be more justifiable is to express all values on the basis of metabolism per square metre of body-surface. The wide use of this method is largely due to the influence of Rubner. Underlying the teaching of this physiologist is the idea that the animal body, being subject to

³ See *J. Physiol.*, 1914, 48; *Proc. Physiol. Soc.*, xxxiii.

Newton's law of cooling, so metabolises that the loss of heat due to cooling may be exactly replaced. On this view, indeed, it is the loss of heat, itself a function of the surface, which definitely determines, in a causative sense, the rate of metabolism; the velocity of chemical change in the tissues is determined directly by the extent of the body-surface. This conception Rubner has elevated to the position of a "physiological law," and upon it as dogma he has built up an elaborate body of doctrine concerning living matter and its energy exchanges.⁴ Recent research seems to show that there is nothing absolute or exclusive about the relation between surface and metabolism. Correlation between the two there is, and must be. When there is a marked difference of size between two warm-blooded animals, as may be the case in individuals of distinct species, it is clear that the smaller, with its relatively much greater surface, and consequent relative greater loss of heat, will demand more rapid oxidations for the maintenance of its body-temperature. The rate of metabolism per unit of weight in the mouse is, needless to say, enormously greater than that in the elephant. What may be questioned is the dogma that loss of heat by the surface is the sole contributing factor—is the essential cause—of metabolism. If it were, if the rate of change in the bodies of all normal individuals were determined by the extent of body-surface alone, then, when placed in similar circumstances, all such individuals would display equal metabolism per square metre of surface. We should then have a simple and definite means for reducing all our observations made on different individuals to a common measure; but there are no relations so definite as these.

The available evidence for the existence of the surface law, read strictly, has, in respect of the animal kingdom as a whole, been recently summarised, and shown to be unsatisfactory by A. Krogh.⁵ Benedict's⁶ recent studies made on men and women seem to be conclusive against it. A glance at the curves given by him, in which the heat production of normal individuals is plotted against their calculated body-surfaces, shows at once how irregular is the relation. The extreme variations found were, in the case of men, from 693 to 958 calories per square metre of surface per twenty-four hours, and, in the case of women, from 633 to 905 calories. The individuals studied by Benedict (eighty-nine men

⁴ "Die Gesetze des Energieverbrauchs," Franz Deutsche, Leipsic and Vienna; "Kraft und Stoff im Hanshatte der Natur," Leipsic, Akad. Verlagsgesellschaft.

⁵ "The Respiratory Exchange of Men and Animals," Monographs of Bio-chemistry, Longmans, 1916.

⁶ *J. Biol. Chem.*, 1915, **20**, 263; *A.*, i, 475; see also *ibid.*, 231, 243, 253; *A.*, i, 474, 475.

and sixty-eight women) were all such as would be called "normal," although they varied somewhat widely in size, age, and occupation. Even within a small, carefully selected group of persons variation in the relation between surface and heat production may be considerable, as is shown by the observations of W. W. Palmer, J. H. Means, and J. L. Gamble.⁷ Benedict in a summary remarks that whilst certain disturbances in the supposed relationship between the two variables may correctly be ascribed to errors in the formulæ used for calculating body-surface, nevertheless the vast bulk of the evidence shows that the variations between metabolism and surface are far outside any possible errors in formulæ. The essential factors which determine the grade of metabolism are the amount of active protoplasmic material in the body and the degree of its activity at any moment. The degree of activity depends on more than one circumstance. This, after all, is what, in the absence of doctrinaire views, we should expect. Surface has an important influence on metabolism, but other influences may be also of sufficient importance to obscure any simple relation between them.

I may now quote some observations made on individuals within more carefully selected groups. Palmer, Means, and Gamble⁸ made their determinations on young medical men closely agreeing in age. They found a variation of 12 per cent. in the heat evolved per square metre of surface. J. R. Murlin and B. R. Hoobler⁹ have studied the energy metabolism of ten hospital children between the ages of two months and one year. They have also calculated, from studies published by others, the average heat evolved per unit of surface in the case of sixty-one American infants. They find the average deviation from the mean value of 39.3 calories per square metre and hour is 11 per cent.; when the results are calculated per kilo. of body-weight the deviation is 12.1 per cent. F. C. Gephart and E. F. Dubois¹⁰ have determined the basal metabolism of normal men, and in discussing their results, together with others available in the literature of the subject, they concluded that among groups of men of varying weight metabolism is more nearly proportional to surface than to weight. They nevertheless admit that the departure of normal men from the average, as based on surface, is such that a given condition cannot be said to be definitely abnormal unless the variation from the mean is of the order of 15 per cent.

If one surveys all that has been published on the subject the conclusion is reached that to calculate metabolism per unit of

⁷ *J. Biol. Chem.*, 1914, **19**, 239; *A*, i, 1914, 1184.

⁹ *Amer. J. Diseases of Children*, 1915, **9**, 81.

¹⁰ *Arch. Int. Med.*, 1915, **15**, 835.

⁸ *Loc. cit.*

surface is somewhat more accurate than to calculate it per unit of weight, especially when the individuals to be compared vary considerably in size. The existence of any "law," involving a constancy of metabolism per unit of surface is, however, imaginary.

The physiologist is, indeed, always face to face with difficulties due to individual variations in men and animals. In metabolism experiments the supposed normal "control" is often the weakest spot. Accuracy in technique does not suffice; the living organism is itself the uncertain factor. The remedy can, however, sometimes be found in patience. If the existence of a metabolic variation of small or moderate degree is to be established, a proportionately large number of individuals must be studied. By comparing, for example, a large number of individuals suffering from severe diabetes with an equal number of normal individuals of the same weight and height, Benedict and Joslin¹¹ have proved conclusively that there is in that disease an increment in metabolism amounting to 15 or 20 per cent.

In the following table I have collected figures from recent papers showing the basal metabolism (defined as above) of men, women, and infants:

Heat per Twenty-four Hours in Calories.

Class.	Per kilo. of body weight	Per square metre of surface.	Observers.
Athletes	26.0	86.3	F. G. Benedict and H. M. Smith.
Untrained individuals com- parable with the above.....	24.4	80.7	F. G. Benedict and H. M. Smith
Women	25.0	77.0	F. G. Benedict and L. E. Emmes.
Men of approximately equal height and weight.....	26.5	81.9	F. G. Benedict and L. E. Emmes.
Normal men of various heights.....	25.9	83.2	F. C. Gephart and E. F. Dubois.
Average of 61 infants.....	64.8	94.3	J. R. Murlin and B. R. Hoobler.

It will have been understood that all the figures previously given relate to metabolism during rest and abstinence. It is a matter of great interest to decide how far this basal metabolism is affected by the mere taking of food. Suppose an individual whose basal metabolism has been determined remain completely at rest, so that the external calls on the body remain as before; will the absorption of food, by itself, affect the rate of metabolism? This,

¹¹ *Carnegie Institution, Publication No. 176, 1912.*

again, is by no means an academic question; for if a considerable degradation of energy occurs during, and as a result of, the assimilation processes, such energy will not be available in support of the specific activities of the tissues. We shall have to deduct it, or some fraction of it, when appraising the real availability of the food eaten.

Rubner during a number of years carried out experiments to test this question. He decided that whereas fats and carbohydrates cause comparatively little rise in metabolism during their digestion, absorption, and assimilation, the case of protein is very different. When protein is eaten, some 30 per cent. of its available energy can, if the experimental conditions are rightly adjusted, be shown to appear as heat during the assimilation period. This Rubner called the specific dynamic action of protein. Its quantitative estimation offers, however, considerable experimental difficulties, and its precise meaning is yet under discussion. Lusk¹² and his co-workers have contributed some interesting papers to the subject during the past year.

The theory of Zuntz that the post-prandial rise in metabolism is due simply to increased activity of the digestive glands and the intestinal musculature is now known to be insufficient, and not supported by the weight of the evidence. Rubner has attributed the rise to the liberation of energy in those intermediary chemical processes which precede the utilisation of protein as a source of energy for the true basal cell metabolism. Roughly speaking, it represents, on Rubner's view, the energy lost during the conversion of part of the protein into carbohydrate and fat. Intermediary products are simply oxidised with the production of extra heat which is in no way involved in the true life processes of the cells. It is, indeed, essential to Rubner's conception of metabolism that we should look on the significant energy exchanges of living matter as fixed and definite in amount, save as affected by varying rates of heat loss. An increase in the supply of material could not affect this essential metabolism. G. Lusk, however, takes another view, returning in a sense to the original teaching of Voit. His experiments have led him to believe that products derived from protein directly stimulate the tissue cells to increased activity. In his earlier papers¹³ he ascribed this action to unaltered amino-acids, but the work published during the past year has led him to the conclusion that it is certain acid intermediary metabolites derived from the amino-acids which actually stimulate the tissues;

¹² *J. Biol. Chem.*, 1915, **20**, vii, A, i, 614; *ibid.*, 555; A, i, 614.

¹³ *Ibid.*, 1912-13, **13**, 158; A., 1913, i, 123.

glycollic and lactic acids, for instance, in the case of glycine and alanine respectively.

Certain experimental results obtained by Lusk may be quoted. Fifty grams of dextrose given to a fasting dog increased the basal metabolism 30 per cent., and 70 grams 35 per cent. There was little difference due to the increase of sugar. "Twenty grams of glycocoll increased it 35 per cent., and the same amount of alanine 32 per cent. Combined, 50 grams of glucose and 20 grams of glycocoll are the glucose equivalent of 66 grams, and yet when they were given together the metabolism increased 56 per cent. Glucose and alanine in similar quantities are a glucose equivalent of 70 grams, and caused an increase of 53 per cent. in the heat production. It is obvious that an increase in the quantity of glucose, when this is given in large amounts, scarcely affects metabolism, whereas when the chemical stimulus from the metabolism products of the amino-acids acts on the cells, in conjunction with a plentiful supply of glucose, the resultant effect is nearly equal to the sum of the two individual influences. This points to a distinct difference between the cause of the specific dynamic action of glucose and that of alanine, which latter is convertible into lactic acid and eventually into glucose."¹⁴

Metabolism is increased by the injection of sugar or fat, but this, according to Lusk, is not because they, or their products, stimulate in any special sense. The increase is simply due to plethora, to the fact that a high concentration of material surrounds the cells. When 10 grams of lævulose are given to a phloridzinised dog there is no increase of metabolism as measured by heat evolution; the whole of the lævulose being excreted as dextrose: but when 12.5 grams of glycine are given, an amount of the amino-acid which also yields 10 grams of dextrose to the urine, there is a large increase of metabolism due to the stimulative action of products intermediate between the amino-acid and the dextrose.

There is a difficulty always present in animal experiments devised to demonstrate the influence of food ingestion or other similar factors on the basal metabolism. It is almost impossible to secure continuous quiescence of the animals. Movements which follow on the process of feeding may be themselves responsible for a large increase in the heat evolved. Needless to say, in the technique used by Lusk this source of error was foreseen and eliminated so far as possible. In the endeavour to eliminate it altogether, C. G. L. Wolf and T. S. Hele¹⁵ have worked with decerebrate

¹⁴ *J. Biol. Chem.*, 1915, **20**, vii-xvii; *A.*, i, 614.

¹⁵ *J. Physiol.*, 1914, **48**, 428; *A.*, 1914, i, 1185.

animals. They show that the injection of glycine into the circulation of decerebrate dogs causes a sharp rise in metabolism, confirming, therefore, the view of Lusk. The actual quantitative value of experiments of this kind is somewhat lessened, however, by the fact that the basal metabolism continuously falls during the experiment owing to the treatment received by the animal.

The Chemistry of Proteins: Some Aspects of Protein Metabolism.

A valuable addition to the technique of protein chemistry is found in F. W. Foreman's¹⁶ method of separating the dibasic acids from the mixture of amino-acids which is obtained on hydrolysing proteins. The calcium salts of glutamic and aspartic acids can be precipitated quantitatively from their aqueous solutions by means of alcohol. When so precipitated from an amino-acid mixture, and liberated from their lime salts, these two acids can be purified by taking advantage of their insolubility in cold glacial acetic acid. Foreman¹⁷ shows that glutamic acid is converted into 1-pyrrolidone-carboxylic acid when its aqueous solutions are boiled, and the change occurs to a small extent even at the temperature of evaporation on the water-bath. To make the above process fully quantitative, therefore, it is probably necessary to carry out all operations at a temperature below 45°. Any addition to analytical methods which are really quantitative cannot but be welcomed by all concerned with the study of proteins, whether from the physiological or chemical point of view. P. Hartley,¹⁸ in an elaborate and careful study of the proteins of ox- and horse-serum, has shown how very successful the method of Van Slyke can be in giving information as to the amounts of various amino-acids contained in any protein, and in enabling us to compare one protein with another. A doubt has often been felt and expressed with regard to the existence of real chemical distinctions between the proteins which have been fractionated from blood serum. The real difference might well be only physico-chemical, one type of protein being easily convertible into another. Various observers, it is true, have obtained more or less conclusive evidence for chemical differences, but the exhaustive study made by Hartley leaves no doubt about the matter, at least as regards a distinction between albumins and globulins. The former contain a notably greater proportion of diamino-acids, and especially, as Hartley demonstrates, of lysine. They contain also perhaps twice the quantity of cystine found in

¹⁶ *Biochem. J.*, 1914, **8**, 463; *A.*, 1914, i, 826.

¹⁷ *Ibid.*, 481; *A.*, 1914, ii, 1205.

¹⁸ *Ibid.*, 541; *A.*, 1914, i, 1206.

the globulins. On the other hand, the different types of globulin agree in respect of their amino-acid content, and the fact that the "pseudo-globulins" and "euglobulins" thus agree lends support to the view of Harriette Chick¹⁹ that the euglobulin of serum is merely a mechanical complex of pseudoglobulin and lipid. The proof that the albumins and globulins of blood are chemically distinct lends great interest to the problem of their physiological differentiation. Have they different origin and different functions?

Hartley's figures, it may be noted, do not show such differences between the corresponding protein fractions from ox blood and horse blood respectively as to supply a basis for those specific characters which other evidence has led us to recognise; but the method used offers, of course, no evidence concerning the grouping of the constituent amino-acids within the molecule of the protein. In this there are infinite possibilities for variation.

So many workers are now employing D. D. Van Slyke's method that it may be well to point out that he has recently introduced some improvements into it, and has recommended a minor modification in the apparatus for his micro-method. He has also published a correction in the formula for calculating the amount of histidine.²⁰

I gave a good deal of space in the Report for 1913 to H. D. Dakin and H. W. Dudley's²¹ views concerning the racemisation of proteins by treatment with alkali, a phenomenon which they explain as an effect of keto-enol tautomerism at the peptide linking.²² The subject seems to me very important, and as a paper criticising Dakin and Dudley's view has recently appeared it will be well to refer to it. P. A. Kober²³ has made a spectrophotometric study of amino-acids and polypeptides, and finds that the absorption of aliphatic acids is only of a general sort in the extreme violet. On the other hand, the aromatic acids (tyrosine and phenylalanine) show marked bands, which may be useful for demonstrating their presence in unknown polypeptides. The chief point in the paper, however, is the demonstration that the spectra of di- and tri-peptides show no special absorption bands in acid or alkaline solution, but only the absorption due to the constituent amino-acids. The fact that this is true of alkaline solutions, in which racemisation is said to occur, yields in Kober's opinion evidence against the occurrence of the tautomeric phenomena which Dakin and Dudley's hypothesis demands. Previous work, that in con-

¹⁹ *Biochem. J.*, 1914, **8**, 404; *A.*, 1914, i, 1145.

²⁰ *J. Biol. Chem.*, 1915, **22**, 281; *A.*, ii, 851; *ibid.*, **23**, 407; *A.*, 1916, ii, 61.

²¹ *Ann. Report*, 1913, 192.

²² *J. Biol. Chem.*, 1915, **23**, 411.

²³ *Ibid.*, **22**, 433; *A.*, ii, 716.

nexion with the acetoacetic series, for example, would lead to the expectation of specific absorption in the case of the peptides if dynamic tautomerism exists in connexion with linkings. Kober further points out that since, according to Fischer and Abderhalden, trypsin digests many, and erepsin all racemic polypeptides, it is remarkable that the "racemised" protein is found to be wholly indigestible. The fact seems to suggest that a more profound change in the molecule has occurred in the process of "racemisation."

Of the remaining criticisms brought forward by Kober I must give space to one only. It will be remembered that on hydrolysis of racemised protein certain of the amino-acids liberated are in the optically inactive form, but others are still active. Dakin suggests that the latter occupy terminal positions in the molecule, where their amino- or carboxy-groups share in no peptide linking. Kober points out that recent evidence has shown that native proteins have few, if any, unlinked groups of this kind. D. D. Van Slyke and F. J. Birchard²⁴ found, by the use of Van Slyke's reagent, that gelatin and casein contain only one type of free amino-groups, namely, that corresponding with the second amino-group of the diamino-acid lysine. This point has been confirmed by Hartley,²⁵ who finds that the free amino-nitrogen of the blood albumins and globulins is, in each case, equal to one-half of the lysine nitrogen. Exactly the same relation has been shown by T. B. Osborne, D. D. Van Slyke, C. S. Leavenworth, and M. Vinograd²⁶ to hold in the case of gliadin, lactalbumin, and the protein of the rice kernel. In eight distinct proteins, therefore, of varying type and origin the second amino-group of lysine appears to be the only one which takes no share in the peptide linkings. The work of the various authors quoted in this connexion well illustrates the progress which is being slowly made towards an understanding of the internal structure of the protein molecule.

T. B. Osborne and L. B. Mendel²⁷ have continued their interesting studies dealing with the varying capacity of individual proteins to maintain the animal or to promote growth. They bring further evidence to show how the relative failure in nutrition of certain proteins can be compensated and removed by the artificial addition of those amino-acids which, in such proteins, are present in relatively too small an amount.

This effect is seen, for example, when cystine is added to casein, and lysine to edestin.

²⁴ *J. Biol. Chem.*, 1913-14, **16**, 530; *A.*, 1914, **i**, 212.

²⁵ *Biochem. J.*, 1915, **9**, 269; *A.*, **i**, 735.

²⁶ *J. Biol. Chem.*, 1915, **22**, 259; *A.*, **i**, 1018.

²⁷ *Ibid.*, **20**, 351; *A.*, **i**, 476.

A point of some importance is to be noted in the exceptional efficiency of lactalbumin as a supporter of growth. In this protein the balance of amino-acids seems to be particularly favourable. When, in Osborne and Mendel's experiments, the protein formed 9 per cent. of the food, individual rats gained some 90 grams on lactalbumin and in the same period gained only 59 grams on casein.

It is clear that the quantitative balance of amino-acids present in the protein eaten will affect, not only the amount necessary to meet the minimal requirements of the animal under various conditions, but also the optimum ratio of the protein in the diet. E. V. McCollum and M. Davis²⁸ have determined the effect of varying ratios of protein. They find that the weights of rats can be maintained on diets in which the proportion of protein, when it is milk protein, is so low as 3 per cent. As it is increased from 3 per cent. to 8 per cent. the velocity of growth of the animals proportionately increases. Proteins from wheat embryo are as efficient as milk protein, but those of the whole wheat grain are inferior. A dietary containing 6 per cent. of the latter has less power of supporting growth than one with 4 per cent. of the former.

Some experiments have been described which illustrate how rapid are the processes of protein metabolism. F. A. Csonka²⁹ has shown that the simpler amino-acids require for their total metabolism under optimal conditions a period of about nine hours' duration. Dextrose when fed, as such, to a phloridzinised dog was found to require nearly the same length of time for its excretion as does the sugar derived from equivalent quantities of glycine and alanine. From this observation the conclusion is drawn that the entire series of metabolic changes leading to the synthesis of dextrose from amino-acids, together with the excretion of the sugar formed occupies a period of time but slightly in excess of that necessary for the simple absorption and assimilation of the corresponding amount of dextrose directly ingested. N. W. Janney,³⁰ quite independently, has shown that proteins themselves, when given to diabetic dogs, are so metabolised that all the extra dextrose and nitrogen are eliminated by the ninth hour after ingestion. In a separate paper Janney combines his own results with those of Csonka, and concludes that the processes involved in the physiological treatment of proteins, including the hydrolysis into amino-acids, the absorption and deamination of these, the synthesis of dextrose and urea and their elimination, all occur in a period that is but little longer than that occupied by the simple process of absorption and elimina-

²⁸ *J. Biol. Chem.*, 1915, 20, 415; *A.*, i, 476.

²⁹ *Ibid.*, 539; *A.*, i, 615. ³⁰ *Ibid.*, 22, 191; *A.*, i, 1026.

tion of dextrose. That the velocity of chemical change in the body can be so great makes clear how difficult is any endeavour to study the individual steps in intermediary metabolism.

The Metabolism of Carbohydrates and Fats.

An important paper from Starling's laboratory by V. H. Moorhouse, S. W. Patterson, and M. Stephenson³¹ deals with metabolism in depancreatized dogs. The research described was clearly very carefully planned and organised, whilst the technique used seems above criticism. The gaseous metabolism was determined in the small respiratory calorimeter devised by Benedict, and special attention was given to the respiratory quotient. The *dextrose:nitrogen* (D/N) ratio was determined, as well as the excretion of the acetone substances. Eight dogs were studied. It is clear that in experimental studies of the kind described in this paper the difficulties due to individual differences in basal metabolism largely disappear. Each animal was studied first when normal and afterwards in the depancreatized condition. It is interesting to find that the rise in total metabolism due to the condition averaged 15—20 per cent., the same figure as that found by Benedict and Joslin for human diabetes.

In its bearing on the still moot question as to whether in the absence of the pancreatic influence there is over-production of sugar, or whether the error is rather in the failure to utilise it, the low respiratory quotient observed in pancreatic diabetes is clearly important. Respiratory quotients may, it is true, be affected by several factors, and conclusions must be drawn from them with due caution; but the authors, having duly considered the possibilities, conclude, no doubt justly, that their experiments on respiration offer very little evidence of the utilisation of sugar in the fully depancreatized dog. The diminished rise, or the absence of any rise, in the value of the quotient after the direct administration of dextrose is certainly strong evidence against utilisation. From the analyses of the urine and their respiratory data Moorhouse, Patterson, and Stephenson calculated the percentage share in the total metabolism taken by protein fat and carbohydrate respectively. When fed on meat the normal dog calls on protein for about 15 per cent. of its metabolism; the diabetic animal uses it to the extent of some 25 per cent. Fats appear, from the results given, to be unexpectedly well dealt with in the animal without a pancreas, and may support by far the greater proportion of the total metabolism. Calculations on the lines just

³¹ *Biochem. J.*, 1915, **9**, 171; *A.*, i, 476.

indicated strengthen the evidence derived from the respiratory quotient in showing how small is the utilisation of sugar.

In the Report for 1913³² I felt justified in saying that current work suggested that the pancreas is concerned in stabilising the carbohydrate sources of the body rather than in promoting the actual utilisation of sugar. The work just quoted seems to point once more in the opposite direction. This problem—certainly one of the most important in pathological chemistry—is extraordinarily elusive.

The somewhat extraordinary observation has been made that the injection of invertase can diminish the excretion of sugar in pancreatic diabetes, and even stop it altogether when the dose is sufficiently large.³³

For an understanding of the chemical changes involved in the utilisation of sugar a knowledge of what is the precursor of lactic acid in muscle is of prime importance. G. Embden³⁴ and his school believe that this precursor is hexose-phosphoric acid. If this be a fact, it is one of great interest, especially in connexion with the synthetic production of the same substance by the yeast cell. The compound has, however, not yet been isolated from the muscle, although Embden and Laquer have fractionated muscle juice and obtained products which contain organically combined phosphorus and a reducing, optically active, component. The chief fact relied on in proof of the nature of the "lactacidogen" is the gradual liberation in expressed muscle juice of lactic acid and free phosphoric acid in equimolecular proportions. When hexose-phosphoric acid is added to the juice the production of lactic acid and phosphoric acid is increased. These researches are of interest, but the results are as yet by no means conclusive.

I may call attention here to the observations of H. W. Dudley concerning the variation of glyoxalase in blood. This catalyst, discovered by Dakin, is concerned, it will be remembered, in the conversion of methylglyoxal into lactic acid. Dudley found that glyoxalase activity, whilst very constant in the blood of a given species, shows definite variations when different species of animal are compared. Those animals which display high glyoxalase values are those with high tolerance for sugar; those with lower values have less well-developed power of assimilating sugar. Such observations tend to confirm the view that methylglyoxal is a metabolite intervening between sugar and lactic acid.

In the intermediary metabolism of fatty acids two lines of

³² *Ann. Report*, 1913, 202.

³³ F. La Franca, *Biochem. Zeitsch.*, 1914, 67, 232; *A.*, i, 24.

³⁴ See series of papers in *Zeitsch. physiol. Chem.*, 1914, 93, 1-144; *A.*, i, 344-346.

chemical change have been demonstrated. The first is the familiar β -oxidation process brought to light by the work of Knoop; the second is a preliminary desaturation occurring in the liver, to which Leathes called the attention of physiologists. The latter has received less attention from experimentalists than the former, but V. H. Mottram has published several papers dealing with the subject. In conjunction with R. Coope³⁵ he has now brought forward evidence to show, first of all, that the transport of the fats from the depots to the liver is a physiological process; it is seen, for instance, as a prominent phenomenon in late pregnancy and early lactation. At these times the livers of rabbits show a definite fatty infiltration with an increase of total fatty acid amounting to 50 per cent. above the normal mean. In a later paper containing abundant experimental data Mottram and Coope³⁶ show that the iodine value of the fats found in the liver lies characteristically between the values for the depot fats and tissue fats respectively. This, of course, is what would be expected if the depot fat is desaturated in the liver before proceeding to the active tissues for utilisation. At the time of parturition the iodine values of the liver fatty acids lie nearer to those of the depot fatty acids than in normal control animals, a fact yielding further evidence of an infiltration of the liver with fats from the depots.

Exogenous Growth Hormones.

I dealt with vitamins at some length in my last Report, but mainly on critical lines. The subject of accessory food factors is a growing one and requires some further reference here.

In April, 1915, E. V. McCollum and M. Davis³⁷ published a paper describing experiments in which growth approximating to the normal rate, together with reproduction and rearing of a portion of the young, was obtained on synthetic dietaries composed of comparatively pure materials. This paper has, not unnaturally, been thought to yield evidence against the existence of unknown accessory food substances, or at least to disprove the assumption that they are essential to growth.

To anyone well acquainted with the circumstances it was quite to be expected that the extraordinarily small amounts of these substances which are sufficient to determine the difference between an efficient and a non-efficient dietary, would lead to the publication of such results as those of McCollum and Davis. It should be understood, however, that these authors, in the papers just referred

³⁵ *J. Physiol.*, 1914, **49**, 23; *A.*, i, 69.

³⁶ *Ibid.*, **49**, 157; *A.*, i, 477.

³⁷ *J. Biol. Chem.*, 1915, **20**, 641; *A.*, i, 617.

to, expressly disclaimed for themselves any desire to put forward their experiments in disproof of the necessity of vitamins or hormones in the diet. Their synthetic dietaries contained lactose, and although Merck's and Kahlbaum's preparations of the sugar were employed it was recognised that such material was possibly not pure enough for experiments of this type.

The later experience of the same authors is most instructive. In extending their experiments, and especially while studying the dietary deficiencies of rice,³⁸ they found that impurity in the lactose was undoubtedly the cause of the growth obtained in their earlier experiments. Using properly purified casein, butter fat, and salts, with dextrine replacing the lactose, they were unable to obtain appreciable growth even during the first month of feeding. That the effect of lactose is not due to its special qualities as a carbohydrate is shown by the varying effect of different samples and also by the fact that when other carbohydrates are employed, as in my own experiments,³⁹ growth is quite normal if the hormone factor be duly supplied.

These authors have now come to the conclusion "that there are necessary for normal nutrition during growth two classes of unknown accessory substances, one soluble in fats and accompanying them in the process of isolation of fats from certain foodstuffs, and the other soluble in water, but apparently not in fats." They themselves,⁴⁰ and also Osborne and Mendel,⁴¹ have published observations showing that certain fats, in particular butter and cod liver oil, promote growth, whilst others, such as tallow and lard, have no such power. Some vegetable fats belong to the former category, some to the latter. This variation is due, not to the essential nature of the fats themselves, but because of a varying content of the hormone factor.

McCollum and Davis now claim that when the remaining constituents of a synthetic dietary are sufficiently well purified the addition of butter fat alone fails to promote growth. The second factor (soluble in water and alcohol) is also necessary. This explains why C. Funk and A. B. Macallum⁴² have been unable to obtain growth when butter alone is added.

No one who properly appraises the evidence now available will doubt for a moment that growth in the animal calls for constituents in the diet which have nothing to do with the energy supply, and, in all probability, nothing to do with the supply of actual structural

³⁸ *J. Biol. Chem.*, 1915, **23**, 181, 231.

³⁹ *J. Physiol.*, 1912, **44**, 425; *A.*, 1912, ii, 779.

⁴⁰ *J. Biol. Chem.*, 1915, **21**, 179; *A.*, i, 617

⁴¹ *Ibid.*, 1914, **17**, 401; *A.*, 1914, i, 619.

⁴² *Zeitsch. physiol. Chem.* 1914, **92**, 13; *A.*, 1914, i, 1017.

material. It should be fully recognised that we have absolutely no knowledge of the chemical nature of such substances. Some negative evidence in this connexion is not without interest. Butter undoubtedly contains a specific growth hormone. Now Osborne and Mendel claim that centrifuged butter fat contains neither nitrogen nor phosphorus,⁴³ although this was doubted by MacCollum and Davis. Funk and Macallum found 0.0008 per cent. of nitrogen.⁴⁴ Osborne and Mendel have proved that when butter fat is fractionally crystallised from alcohol all the specific growth factor remains in the less crystallisable fraction of low melting point, that is, in the butter "oil."⁴⁵ Osborne and A. J. Wakeman⁴⁶ have estimated the phosphorus in this fraction at 0.0006 per cent. These figures are so small that it seems unlikely that the growth substances contain either nitrogen or phosphorus, but it would be dangerous to dogmatise on the evidence available. I feel that the name I have placed at the head of this section is, so long as we are ignorant of the nature of these substances, to be preferred to that of vitamins.

The Enzymes of Blood and the Action of Serum on other Enzymes.

The Abderhalden reaction, which was discussed in my last Report, has formed the subject of a number of papers published during the year. It has also stimulated interest in the blood ferments generally.

As regards the reaction itself, opinions still differ as to its specificity and trustworthiness. Some report favourably.⁴⁷ One observer found that the optical and dialysis methods harmonised in twenty out of twenty-eight cases, and that in nineteen of these they were in agreement with clinical diagnosis.⁴⁸ It is stated that when different organs in the body are ligatured off from the circulation and the serum then tested by Abderhalden's methods, a proteolytic ferment is found in the blood. This is specific for the organ which was cut off from the circulation, and does not act on the proteins of other organs.

On the whole, however, the weight of the evidence is against the specificity of the Abderhalden reaction, and doubt has been thrown on the accepted views as to its nature. It has been claimed, for instance, that normal serum shows non-specific proteolytic activity so soon as its content of anti-trypsin is removed.⁴⁹ In

⁴³ *J. Biol. Chem.*, 1915, **20**, 382; *A.*, i, 477.

⁴⁴ *Loc. cit.* ⁴⁵ *Loc. cit.*

⁴⁶ *Ibid.*, 1915, **21**, 91; *A.*, i, 623.

⁴⁷ Compare J. Rosenbloom, *Biochem. Bull.*, 1914, **3**, 373; *A.*, i, 42.

⁴⁸ G. Hülsen, *Biochem. Zeitsch.*, 1914, **67**, 277; *A.*, i, 340.

⁴⁹ J. and K. M. Scott, *Proc. Soc. Expt. Biol. Med.*, 1915, **12**, 137; *A.*, i, 472. also J. Bronfenbrenner, *Biochem. Bull.*, 1915, **4**, 87; *A.*, i, 626.

pregnancy, on this view, the anti-substance combines with the placenta antigen, and so sets free the one and only protease which is present in all serum. In the Abderhalden test it is not the placental substrate which is digested, but the serum itself. Others claim that normal serum has a weak proteolytic activity of its own, even when it has received no treatment of any kind. This increases with age of the individual, and is also increased in conditions other than pregnancy.⁵⁰

The blood undoubtedly contains an amylase, and starch injected into the circulation is saccharified.⁵¹ The amount of amylase present does not, however, depend on the diet or feeding habits of the animal, for the serum of the goat, which is entirely herbivorous, has only about one-twelfth the amylolytic activity of that of the dog or cat. The ferment is almost certainly derived from the pancreas and salivary glands. Pancreatic disease leads to a diminution in the blood- and urinary-amylase.⁵² For some reason removal of the pancreas also reduces the nuclease content of the blood and tissues.⁵³

The factor in serum which accelerates the fat-splitting power of pancreatic juice (auxolipase) is distinct from the co-enzyme with the same action contained in the pancreatic extracts, since it is non-dialysable. It is, however, thermostable. Mellanby and Woolley have suggested that serum activates lipase merely because it contains anti-trypsin; this prevents the destructive action which trypsin otherwise exerts on the fat-splitting ferment. This does not seem to be the case. K. Isuji⁵⁴ and J. A. Shaw-Mackenzie⁵⁵ have independently shown that there is no parallelism between the amount of anti-trypsin in the serum and its power of accelerating lipolysis. The latter observer finds also that when the serum is heated to a temperature sufficient to destroy anti-trypsin it still exhibits marked influence on lipase.

The frequency with which the serum affects, in one sense or another, the velocity of enzyme reactions is a noteworthy physiological fact. The last case to be studied is that of urease. The sera of various animals greatly accelerate the action of the ferment of the soja bean. Human serum increases it about eight-fold, and the amount of the auxo-urease is here very constant, being seemingly unaffected by the most varied pathological conditions.⁵⁶

⁵⁰ L. H. Sloan, *Amer. J. Physiol.*, 1915, **39**, 9; *A.*, i, 1077.

⁵¹ H. McGuigan and C. L. von Hess, *ibid.*, **36**, 359; *A.*, i, 186.

⁵² C. E. King, *ibid.*, 1914, **35**, 301; *A.*, i, 35; V. Stavraki, *Biochem Zeitsch.*, 1915, **69**, 370; *A.*, i, 735.

⁵³ Stavraki, *loc. cit.*

⁵⁴ *Biochem. J.*, 1915, **9**, 53; *A.*, i, 473.

⁵⁵ *J. Physiol.*, 1915, **49**, 216; *A.*, i, 473.

⁵⁶ R. Neumann, *Biochem. Zeitsch.*, 1915, **69**, 134; *A.*, i, 613.

An active preparation can be prepared by precipitating sheep's serum with alcohol and extracting the precipitate with water. It is remarkable that the substance thus obtained is, unlike the natural auxo substance, dialysable and not destroyed by peptic digestion.⁵⁷

Internal Secretions.

It is now some time since attention was given in these Reports to the organs of internal secretion. No progress of a startling sort has been made during the last year or two, but some useful work may be chronicled. Attention has been given in particular to the pituitary body, the importance of this gland to the organism being now very clear. The history of our knowledge concerning the organ was brought up to date by Professor Halliburton in his Report for the year 1909. On the chemical side the facts known up to 1913 are given by Barger in his very useful book, "The Simpler Natural Bases."⁵⁸

To the earlier-known physiological effects of extracts of this gland (a direct stimulation of involuntary muscle and a diuretic action) there have been more recently added a power to increase the flow of milk and stimulate the ovary. These last functions have received some attention during the year. The galactagogue action was first observed by Ott and Scott,⁵⁹ and was studied in some detail by J. Hammond.⁶⁰ Hammond found that the injection of pituitary extracts produce an immediate increase in the flow of milk which is followed by a period of decreased flow, the actual daily yield being only slightly increased as the result of the injection. The milk formed is particularly rich in fat. This author believed that the effect was not on the muscles of the mammary gland, but on the epithelium cells, a true secretory stimulus. R. L. Hill and S. Simpson⁶¹ found that when ox-pituitary extract is injected into the goat there is a marked increase in the amount of milk obtained fifteen minutes later; the next milking, a few hours later on, shows a corresponding decrease. The same authors tested the effect of pituitrin on a human subject.⁶² The injection of 20 milligrams of the dried infundibular portion of the gland into a woman during lactation was followed in ten minutes by a noteworthy increase in the amount of milk secreted. The milk with-

⁵⁷ M. Jacoby and N. Umeda, *Biochem. Zeitsch.*, 1915, **68**, 23; *A.*, i, 186.

⁵⁸ Monographs on Biochemistry, Longmans, 1914.

⁵⁹ *Therap. Gazette*, 1911.

⁶⁰ *Quart. J. expt. Physiol.*, 1913, **6**, 311; *A.*, 1913, i, 1133.

⁶¹ *Ibid.*, 1914, **8**, 103; *A.*, i, 45.

⁶² *Amer. J. Physiol.*, 1914, **35**, 361; *A.*, i, 45.

drawn after the injection was rich in fat, containing 5.5 per cent. as against 3.5 per cent. in the milk produced without pituitrin. In the milk produced a day after the injection the fat was still somewhat above the normal.

The authors just quoted hold, like Hammond, that the action is on the secretory cells, and not on the muscular tissue, since barium chloride, a specific stimulant of muscle, causes no milk flow. E. A. Schäfer,⁶³ however, criticises their conclusions, and maintains that the discharge of milk is due to the contraction of the smooth muscle in the walls of the glandular alveoli. A second injection of pituitrin does not, he states, yield any milk until time has been allowed for fresh secretion to accumulate. It is not certain, Schäfer holds, that barium chloride acts on the muscle of the gland, whereas pituitrin is known to act powerfully on most, if not all, smooth muscles. W. L. Gaines,⁶⁴ experimenting with goats, confirms Schäfer's conclusions. L. A. I. Maxwell and A. C. H. Rothera,⁶⁵ however, strongly support the view that pituitrin is a true secretory stimulant. They point out that when injections are given immediately after milking, the amount of milk immediately obtained is too large in amount to arise from a further emptying of the exhausted gland by muscular contractions. On measuring the intramammary milk pressure they found that the rise in this due to pituitrin is a gradual process, and the increased pressure is long maintained. If the action were merely on muscles a rapid initial rise would be expected, followed by a fairly rapid fall. It is clear that the nature of the mechanism of the action is still uncertain, and that some crucial experiment must be devised capable of giving a definite decision. It would certainly be of interest to be sure that the gland possesses a specific action on mammary gland cells. The economic importance of the artificial use of pituitrin in this connexion is probably negligible, since the immediate increase in the milk would seem to be always followed by a compensatory fall.

Several observers have shown during the last year or two that pituitary extracts have a stimulating action on the ovary. This has led certain American workers to try if it be possible by administering pituitrin to increase the output of eggs by the domestic fowl. Injection of extracts of the anterior lobe into the abdominal cavity during the period of moulting had no effect,⁶⁶ but the same part of the gland when taken from growing mammals and given by

⁶³ *Quart. J. Expt. Physiol.*, 1915, **8**, 399; *A.*, i, 191.

⁶⁴ *Amer. J. Physiol.*, 1915, **36**, 360; *A.*, i, 191.

⁶⁵ *J. Physiol.*, 1915, **49**, 483; *A.*, i, 1033.

⁶⁶ R. Pearl and F. M. Surface, *J. Biol. Chem.*, 1915, **21**, 95; *A.*, i, 620.

the mouth is stated to have produced a noteworthy increase in egg production.⁶⁷

We have as yet no definite knowledge as to the chemical nature of the active principle or principles contained in the pituitary body. The evidence seems to point to the existence of more than one. Farbwerke vorm. Meister, Lucius & Brüning by the use of phosphotungstic acid as a precipitant obtained a crystalline sulphate,⁶⁸ which Fühner⁶⁹ afterwards separated by fractional crystallisation into four different substances, all of which seemed to contribute to the activity of the gland. F. Hoffmann, La Roche & Co. have also patented a method of obtaining a crystalline product. During the preparation of this last product evidence of more than one active principle also came to light. A substance acting on the intestines appeared to be more soluble in chloroform than another acting on the blood vessels and uterus.⁷⁰ A. Hunter's⁷¹ work seems also to show that different actions of the gland may be due to distinct substances.

Extracts of the organ give Pauly's histidine reaction, and there is considerable probability that one at least of the active constituents is a histidine derivative. T. B. Aldrich was unable to obtain other histidine reactions, but, as H. Pauly⁷² points out, the diazo-reaction is twenty to fifty times more delicate than any other, and its significance should not be disregarded because others fail. M. Guggenheim⁷³ calls attention to resemblances between the action of the pituitary substance and that of acetylcholine. He believes that the gland contains an ester-like derivative of an alkanolamine with an acetyl residue.

In about 10 per cent. of the glands removed from the ox colloid masses are found between the two lobes. F. Fenger⁷⁴ has examined these, but finds the substance is without physiological action. I only mention his paper to record the fact that in preparing the colloid for study he used material derived from at least 30,000 cattle. This illustrates how difficult it may be to work at some details of tissue chemistry for those who are not, like the author quoted, in touch with such sources of supply as the firm of Armour of Chicago!

When iodine was first discovered in the thyroid gland by

⁶⁷ L. N. Clark, *Amer. J. Physiol.*, 1915, **22**, 485; *A.*, i, 1031.

⁶⁸ See *A.*, 1914, i, 756.

⁶⁹ *Zeitsch. f. d. ges. expt. Med.*, 1913, **1**, 397.

⁷⁰ See *A.*, i, 857.

⁷¹ *Quart. J. Expt. Physiol.*, 1914, **8**, 245, 267.

⁷² *Zeitsch. physiol. Chem.*, 1915, **94**, 427; *A.*, i, 917.

⁷³ *Biochem. Zeitsch.*, 1914, **65**, 189; *A.*, 1914, i, 1021.

⁷⁴ *J. Biol. Chem.*, 1915, **21**, 288; *A.*, i, 739.

Baumann, it was generally assumed that the organic iodine compound present was responsible for the peculiar activities of the organ. Later on, for a period, this was doubted, in particular because it was believed that glands known to be normal in function could be shown to be free from iodine. Of late evidence has accumulated to show that the earlier opinion was right. Improved methods of detecting the halogen have demonstrated its presence where it was missed before, and although the amount present in the organ varies through a wide range it is probably never absent. A. T. Cameron⁷⁵ in three very full reports has given an account of the distribution of iodine in the tissues of animals and plants. Many interesting data are collected or supplied. All marine species of animals contain iodine. As advances in evolution are made there is more differentiation in the distribution and probably less total iodine in the whole organism. Much of the material which has been found to contain the element is in the nature of an external secretion (a secretion on the outer surface of the body). Of vertebrate tissue the thyroid alone is of importance in connexion with the storage of iodine. Fenger has found that human foetal thyroid contains iodine during the last three months of pregnancy.⁷⁶ The limits in the amounts found in dry thyroid are 0.01 and 1.16 per cent.⁷⁷ There seems little doubt that the main cause of the variation is to be sought in the diet.

During the administration of iodides (to dogs) the thyroid gland is the only organ retaining organically combined iodine. It is the only organ capable of transforming the inorganic halogen into iodine-protein compounds and of thus acting as a storage for iodine in the body.⁷⁸ The quite special affinity of thyroid tissue for the element is demonstrated by the observations of D. Marine.⁷⁹ In one set of experiments various isolated organs were perfused with a mixture of blood and Ringer's solution to which potassium iodide was added. Only the thyroid retained the iodine, and this only during the period of its survival. The dead tissue retained none. In other experiments iodides were fed to the living animal. As much as 18.5 per cent. of the iodide given was retained in the thyroid, with none elsewhere, and this when the weight of the gland was to the body-weight in the ratio of only 1 to 687.

⁷⁵ *J. Biol. Chem.*, 1914, **16**, 465; *A.*, 1914, *i*, 227; *ibid.*, 1914, **18**, 335; *A.*, 1914, *i*, 1154; *ibid.*, 1915, **23**, 1. ⁷⁶ *Ibid.*, **20**, 695; *A.*, *i*, 620.

⁷⁷ The highest figure refers to the gland of an elasmobranch fish. In the mammal the maximum found is 0.629 per cent. (dog's thyroid). On this subject see also Hunter and Simpson, *J. Biol. Chem.*, 1915, **20**, 119; *A.*, *i*, 192.

⁷⁸ F. Blum and R. Grützner, *Zeitsch. physiol. Chem.*, 1914, **92**, 260; *A.*, *i*, 343.

⁷⁹ *Proc. Soc. expt. Biol. Med.*, 1915, **12**, 132; *A.*, *i*, 478.

These recent experiments confirm very fully the fact that there exists within the thyroid a specialised chemical mechanism for the arrest of the halogen in an organic form. The proof of so specific a property in a particular tissue has general bearings, and makes it easier to believe in highly selective tissue affinities in other cases where the concrete chemical facts are less easy to demonstrate.

It would seem from the work of J. M. Rabe, J. Rogers, G. G. Fawcett, and S. P. Beebe⁸⁰ that stimulation of the vagus can undoubtedly cause discharge of iodine compounds from the gland into the blood, an important observation in connexion with the relation between the nervous system and hyperthyroidism.

If iodo-protein compounds are responsible for the physiological properties of the organ, it would be interesting to know whether these properties are attached to the complex as a whole or whether they are more particularly due to some amino-acid grouping within the protein molecule; the group, or groups, that is, with which the iodine is directly associated. From what we know of artificial halogen-proteins we should expect the iodine to be associated with one or more of the aromatic groups. It is noteworthy, therefore, to find that certain effects produced by the thyroid are also brought about by di-iodotyrosine. Thus M. Morse⁸¹ has shown that acceleration of the metamorphosis in tadpoles which is seen on feeding with the gland is also produced when 3:5-di-iodotyrosine is given. The metamorphosis may occur in three days instead of requiring the normal fortnight. C. H. Frazier and M. M. Peet⁸² state that di-iodotyrosine acts like extracts of the gland in slowing the rate of secretion of cerebrospinal fluid.

E. C. Kendall⁸³ claims, on the other hand, to have shown that part at least of the iodine of the gland is in association with the indole nucleus. After hydrolysing the gland tissue with 1 per cent. sodium hydroxide in 90 per cent. alcohol he isolated a product identified as di-iodohydroxyindole. This is stated to have given results on administration similar to those of thyroid feeding. If the observation should be confirmed it is certainly one of great interest.

Uric Acid in Blood.

I have devoted no section to purine metabolism this year as, for the most part, the work done is unimportant, but it is essential to note a paper by S. R. Benedict⁸⁴ dealing with the

⁸⁰ *Amer. J. Physiol.*, 1914, **34**, 72; *A.*, 1914, i, 622.

⁸¹ *J. Biol. Chem.*, 1914, **19**, 421; *A.*, i, 45.

⁸² *Amer. J. Physiol.*, 1915, **38**, 93; *A.*, i, 737.

⁸³ *J. Amer. Med. Assn.*, 1915, **64**, 2042; see also *J. Biol. Chem.*, 1915, **20**, 501; *A.*, i, 600.

⁸⁴ *J. Biol. Chem.*, 1915, **20**, 633; *A.*, i, 612.

existence of conjugated uric acid in mammalian blood. If the findings of the author are confirmed and shown to have general bearings they will considerably modify all future studies of uric acid in health and disease. Using a colorimetric method previously described by himself, Benedict found that ox blood yields on the average half a milligram of uric acid. This we should have hitherto recognised as being the total content of that substance. It was, however, accidentally observed that after certain treatment of the blood the uric acid increased to a remarkable degree, and finally it was discovered that if the blood proteins be removed with colloidal iron and the filtrate concentrated in the presence of hydrochloric acid the amount of uric acid found may show an increase over the "free" acid of as much as 1000 to 1300 per cent. It was then found that the combined uric acid is gradually liberated in the blood by the action of an enzyme present. Ox blood containing only 0.5 milligram when fresh yielded 7.5 milligrams after remaining for a fortnight in the presence of antiseptics. Whatever the nature of the combination may be in which uric acid exists it is certainly not associated with protein. The remarkable fact next came to light that whilst in the mammalian blood the uric acid is wholly contained in the corpuscles, in bird's (chicken's) blood it is almost entirely confined to the serum. These relations have not been suspected hitherto. It is clear that they have important bearings on the physiology of purin metabolism. Benedict wisely avoids speculation on the subject until further experiments have been made, but it is tempting, at any rate, to believe that uric acid which can be further metabolised circulates in combination, whilst that which is to be directly eliminated circulates free.

Concentration of Antigens.

G. S. Walpole⁸⁵ has described very valuable methods for standardising collodian filters suitable for "ultrafiltration" and pressure dialysis operations. Certain members of the standard series, defined by their weight and content of nitrogen per sq. cm., are especially valuable for separating antigens. They are impermeable to all such, although allowing water-salts and simpler molecules to pass freely. In a paper published with A. T. Glenny he illustrates the use of his method. In particular, a process for the concentration and purification of diphtheria toxin is fully described. The paper makes it clear that a very definite advance in technique has been reached. The membranes are impermeable to enzymes, but allow to pass secretin, the pituitary active principle, the co-enzyme of zymase, and the toxic constituent of Witte's peptone.

F. G. HOPKINS.

⁸⁵ *Biochem. J.*, 1915, **9**, 284; *A.*, ii, 549.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

THE year 1915 has not differed much from previous years either as regards the number of investigations published or the importance of the results obtained, and no results of obviously outstanding interest have to be recorded.

Among publications may be mentioned the "Journal of the Association of Official Agricultural Chemists," which will contain the Proceedings of the Annual Conventions, formerly published as Bulletins of the Bureau of Chemistry, U.S. Department of Agriculture; "Soils: their Properties and Management," by T. L. Lyon, E. O. Fippin, and H. O. Buckman; "Soils and Plant Life as Related to Agriculture," by E. J. Russell; and "Die Ernährung der landwirtschaftlichen, Kulturpflanzen," by W. Schneidewind.

The Atmosphere.

A series of analyses of daily collections of rain-water, extending over fourteen months, has been made at Melbourne and at Canterbury, six miles distant, in which the amounts of nitrogen as nitrates and nitrites were estimated.¹ At Canterbury the total oxidised nitrogen amounted to 0.503 kilo. per hectare per annum, and the relation of nitric to nitrous nitrogen was about 10:1. In the summer months the concentration of nitrous nitrogen was less, and in winter much higher, than the average for the year, whilst the nitric nitrogen was highest in the autumn and summer, and lowest in winter.

Although local thunder-storms increase the amounts of oxidised nitrogen in the air, their effect is comparatively slight, and some of the highest results were obtained when there was no storm. The highest amounts of oxidised nitrogen occur when the air through which the rain falls has circulated over an area which has, for a long period, been subjected to continuous electrical discharges. The rain collected during tropical storms of the extreme summer type brought down 0.039 kilo. of oxidised nitrogen per hectare; in the usual summer type of tropical depression the average amount was 0.026 kilo., and in spring and autumn depressions 0.018 kilo.

¹ V. G. Anderson, *Report Brit. Assoc.*, 1914, 338; *A.*, i, 860; *Quart. J. Roy. Met. Soc.*, 1915, 41, 99.

Very different results were obtained with antarctic depressions, when the average amounts of oxidised nitrogen varied from 0.0017 to 0.0046 kilo. according to the type.

It seems doubtful whether the conclusions drawn from the relation of nitrous to nitric nitrogen are quite justified. Whilst several results obtained in other localities also show higher amounts of nitrites in the summer than in the winter months, this does not invariably seem to be the case. It must also be borne in mind that the rain falling after a period of fine weather will wash out the nitrates accumulated during the whole period, whilst the nitrous acid, unless present in the more stable form of salts, will only represent the last day or two.

The investigation, which is the first satisfactory attempt to correlate the amounts of constituents found in rain and the weather conditions, seems to promise interesting results, and it shows the desirability of adequate meteorological data in connexion with investigations of air and rain.

At Ottawa the series of analyses of rain-water, now in its eighth year, has been continued,² and estimations of organic, nitric, and nitrous nitrogen, ammonia, chlorides, and sulphates have been made at Mount Vernon, Iowa.³

Soils.

In addition to the movements of water in soils caused by gravitation and capillarity, it has been shown that soil water is subject to osmosis.⁴ Experiments were made in which a column of soil, 6.5 cm. deep, was employed as semi-permeable membrane, and a concentrated soil extract as solution. Results were obtained showing an osmotic pressure equal to that of a column of water about 3 m. high. The soil resembles the usual semi-permeable membrane, being probably in a colloidal state, and in absorbing water more readily than a soil solution, so that the movement is towards the soil solution as the liquid least absorbed.

Investigations of Japanese soils⁵ have shown that when steeped in different solutions the increase in volume varies according to the substance employed, being greatest in alkalis, next in acids, then in solutions of salts and in water, and least in alcohol. The gel forms vary according to the reagent employed, and the soil constituents from which they are formed are not uniform substances. When soils are dialysed and the residues compared

² F. T. Shutt, *Trans. Roy. Soc. Canada*, 1914, [iii], 8, 83; *A.*, i, 636.

³ W. K. Knox, *Chem. News*, 1915, 111, 61; *A.*, i, 204.

⁴ C. J. Lynde, and J. V. Dupré, *Proc. Roy. Soc. Canada*, 1914, [iii], 8, 133; *A.*, i, 762.

⁵ T. Tadokoro, *J. Coll. Agric. Tohoku*, 1914, 6, 27, 117; *A.*, i, 636.

with the original soils it is found that the differences are very slight; the colloids which dissolve in water are, therefore, not of importance in this connexion.

In accordance with van Bemmelen's results, it is shown that the powers of adsorption of dyes and nutritive solutions possessed by soils diminishes with dilution. The adsorption of dyes is closely related to the changes in volume and to the hygroscopicity, all being intimately connected with the amounts of solid colloids present. The power of absorbing ammonia, on the other hand, seems to be more complicated, and has no regular relation to the adsorption of dyes, the increase in volume, and the hygroscopicity, which depend only on the surface of the colloid portion of the soil. The coefficient of ammonia absorption is greater in normal ammonium phosphate than in normal ammonium chloride, probably owing to the liberated phosphoric acid forming insoluble compounds with aluminium.

Comparing different kinds of soils it is found that the increase in volume and the adsorption of dyes is greatest in humus soils, less in clay soils, and least in sandy soils. In the case of hygroscopicity the order of humus and clay soils is reversed.

With mineral-acid soils the increase in volume is greater than with neutral soils containing plenty of humus, but it is sometimes less than that observed with neutral soils deficient in humus. The differences in increase in volume observed with different reagents are much greater in the case of mineral-acid soils than with neutral soils, indicating that the colloids of the acid soils have mobile, unstable forms. Hygroscopicity does not seem to vary much in the different acid soils as compared with the neutral soils. The adsorption of dyes and absorption of ammonia are usually greater in mineral-acid than in neutral soils; there is, however, no great difference between the lowest results obtained with the former and the highest obtained with the latter.

With reference to the acidity of upland soils containing very little organic matter, which has been attributed to absorption of bases by colloids, it has been pointed out that the silicates react with soil solutions forming a soluble hydroxide, or salt, which is either assimilated by plants or else removed in drainage, and a comparatively insoluble acid silicate.⁶ The failure of acid soils to take up equivalents of the different bases from salt solutions, which is partly responsible for the colloid theory, is due to the sparing solubility of the acid silicates and their neutralisation products.

When the opportunity for secondary reactions is eliminated as far as possible by treating very finely powdered soil with large

⁶ E. Truog, *Science*, 1915, N.S., 42, 505.

amounts of salt solution for a short time, it is shown that very nearly equivalent amounts of the different bases are taken up.

Soil acidity can be estimated by stirring 25 grams of soil, moistened with 35 c.c. of water, with an excess of barium hydroxide solution for one minute, after which carbon dioxide is passed through. The whole is then evaporated to dryness and the excess of barium hydroxide ascertained by estimating the carbonate. The fact that either sodium, barium, or calcium hydroxide may be employed is evidence that the acidity is due to acid, and not to colloids.

The results of a number of experiments with different soils⁷ showed that in order to obtain a knowledge of the amount of calcium carbonate which should be applied, it is desirable to estimate the acidity rather than the carbonates present. Carbonates may be absent in neutral soils and present, locally, in acid soils. It was found that addition of calcium carbonate to soils, according to the acidity as indicated by the bicarbonate method, at once showed increased ammonia production and greater plant growth in pot cultures. Calcium carbonate and oxide have the same effect until the point is reached at which the acidity is neutralised, after which the oxide has partial sterilisation effects, to which reference will be made later on.

Some interesting results were obtained by estimating the acidity of different samples of the same uncultivated soil which were selected according to the predominating plants. Taking the extremes, it was found that the percentage amount of lime required by the soil with wild white clover was 0.22, whilst the sorrel soil showed a requirement of 0.53 per cent. The soils with *Festuca*, gorse, and Yorkshire fog occupied intermediate positions.

The results of pot experiments in which clover was grown in a sandy clay loam, showing a lime requirement of about 0.06 per cent., indicated that low yields are obtained when a great excess of precipitated calcium carbonate is applied.⁸ High results were obtained, however, when calcium was applied as silicate (wollastonite), with magnesium silicate (serpentine), and with a mixture of calcium and magnesium silicates. In a silty loam of the same acidity the growth was in each case very much less; much the highest results were obtained with the mixed silicates.

Investigations on the calciphobe behaviour of lupines have sometimes given conflicting results, and it has not yet been possible to obtain any quite satisfactory explanation. The results of experiments extending over three years⁹ seem to show, in agreement

⁷ H. B. Hutchinson and K. McLennan, *J. Agric. Sci.*, 1915, **7**, 75.

⁸ W. H. MacIntyre and L. G. Willis, *J. Ind. Eng. Chem.*, 1914, **8**, 1005; *A.*, **i**, 52.

⁹ T. Pfeiffer and E. Blanck, *Mitt. landw. Inst. Univ. Breslau*, 1914, **7**, 201; *A.*, **i**, 201.

with results obtained in earlier investigations, that one injurious effect of the application of calcium carbonate is to prevent the assimilation of sufficient iron; there is, however, no doubt that other injurious actions take place. Limestone is found to be less injurious to lupines than precipitated calcium carbonate, and calcium sulphate, although injurious, is less so than carbonate; lupines manured with gypsum take up less calcium than when carbonate is applied. Calcium nitrate has an unfavourable effect when applied along with the carbonate; potassium nitrate has, however, the same effect, so that the increased injury must, in both cases, be attributed to the physiologically alkaline reaction of the nitrates.

Applications of limestone to lupines has a retarding effect on the formation of root-nodules, and consequently on nitrogen assimilation; it also has a marked effect on the assimilation of phosphoric acid, except when ammonium sulphate is applied as well.

Soil Gases and Aeration.

An examination of the air of soils collected at a depth of 15 cm. has shown that the free air is very similar in composition to atmospheric air, but that it contains more carbon dioxide and correspondingly less oxygen, and shows greater variations in composition.¹⁰ The sum of the percentages of the carbon dioxide and the oxygen is usually only slightly less than that of the atmosphere; there is, however, a perceptible fall in the amounts of oxygen during periods of active nitrification, and a still greater fall in water-logged soils.

This free air does not represent the whole of the gases present in soils. By keeping a mercury pump at work for several days after the flask containing the soil has been exhausted, a further small amount of gas is obtained from the water and colloids of the soil, consisting mainly, and finally almost exclusively, of carbon dioxide with very little, if any, oxygen. These results suggest the possibility of simultaneous aerobic and anaerobic bacterial activity in soils.

Confining attention to the free air of the soil, it is shown that the fluctuations in composition depend mainly on fluctuations in bacterial activity, and that the curves are similar to those showing the amounts of nitrate and the numbers of bacteria. The maximum values occur in the late spring and again in autumn, whilst the minimum values occur in summer and winter. In the autumn the bacteria increase first, then the carbon dioxide, and finally the nitrates. From November to May the curves closely follow those for the temperature of the soil, which seems to be the dominating

¹⁰ E. J. Russell and A. Appleyard, *J. Agric. Sci.*, 1915, 7, 1; 4, i, 635.

factor, and from May to November they follow the rainfall, and, to a less extent, the soil moisture curves, the beneficial effect of rain, apart from soil moisture, probably being due to the dissolved oxygen.

Grass-land usually contains more carbon dioxide and less oxygen than arable land; there was, however, no evidence to show that a growing crop has any marked influence in increasing the amount of carbon dioxide in the soil air. Weather conditions, such as barometric pressure, wind velocity, and variations from the mean temperature, do not seem to have any important influence on the atmosphere of the soil.

In India a very comprehensive investigation of soil gases has been made in which the total amounts of soil gas and the amounts of its various constituents (including argon, hydrogen, and methane) were estimated in samples obtained under different conditions.¹¹

Experiments with Bihar alluvium showed that whilst the volume of water was increased during rains to about four times the amount previously present, the volume of gas is usually not decreased to one half.

The gases from swamp rice-land showed high ratios of nitrogen to argon, indicating liberation of soil nitrogen. Considerable amounts of hydrogen were found, as well as some methane, whilst the percentage of oxygen was very low.

Soil samples obtained near roots of different crops, yielded gases containing very large amounts of carbon dioxide, very small amounts of oxygen, and almost always some hydrogen, but no methane. Hydrogen was found near the roots of three different crops—san hemp, indigo, and maize.

As regards the influence of nitrification on the soil oxygen, it is shown that after abundant nitrification, resulting from a heavy rain in June, the soil contained almost the same amount of oxygen as before. From these results, and some others obtained in experiments on nitrification in closed vessels, with both small and large amounts of air, the conclusion is drawn that the diffusion of gases in soils is sufficiently rapid to prevent a deficiency of oxygen. It should, however, be borne in mind that the rain must have contributed a good deal of dissolved oxygen, and that the water percolating through the soil will draw into the soil large amounts of air from above. The assumption that aeration, as an important result of tillage, is put out of court by these results, and that the benefits of tillage must exclusively be due to other effects, does not seem to be very probable.

¹¹ J. W. Leather, *Mem. Dept. Agric. India, Chem. Ser.*, 1915, 4, 85; *A.*, 1916, i, 110.

It has been found in Russia¹² that the best crops of winter cereals are obtained after the so-called black fallow and the April fallow, and that a definite connexion exists between the manner of working the fallow and the humidity of the soil. In order to ascertain the effects of the different types of fallow on aeration, four types were selected for investigation: the black fallow, which begins in the autumn, the April fallow, and two June fallows, one of which is characterised by the soil being much trodden by cattle put on to graze. In soil samples collected from June to September 1st, it was found that the black fallow soil contained 51—81 c.c. of oxygen per litre, April fallow soil 65—81.4 c.c., and the June fallow soils, without and with cattle, 52—65 c.c. and 32—48 c.c. respectively. At the time of sowing (August 1st) the relative amounts of oxygen with the four fallows were 100, 107, 86.5, and 54.2 c.c. In April, samples of the soil under rye were examined in order to show the effect of the winter season, and it was found that the amounts of oxygen in the soils (taking the fallows in the same order as before) had fallen to 49.5, 45.4, 43.5, and 24.0 c.c. per litre of soil.

Further experiments on the influence of temperature, diffusion of gases, percolation of water, and wind on the composition of the soil air showed that percolation of water during periods of rain is the most active factor.

In the alluvial soils of the Indo-Gangetic plain aeration is difficult, owing to the readiness with which hard crusts are formed after heavy rain or irrigation, and in some parts to the rise of the water table to within a few feet of the surface.¹³ The crops in these regions frequently suffer from asphyxiation, and can only be saved by breaking the crust and aerating to as great a depth as possible. Deficient aeration has also been observed on similar soils under quite different climatic conditions. When green manuring is adopted, the necessity for aeration is still more marked, and it is suggested that the injury to fruit trees caused by grass is due to excessive production of carbon dioxide. There is, however, no direct evidence to support this view.

Under other conditions, it has been found that green manuring, besides acting as a manure, actually increases, indirectly, the supply of oxygen in the soil.¹⁴ In swamp rice soils it has been shown that the surface becomes covered by an organised film con-

¹² A. G. Dojarenko, *Bull. Agric. Intell. Plant Diseases*, 1915, **6**, 1299.

¹³ A. Howard and G. L. C. Howard, *Bull. Agric. Research Inst. Pusa*, 1915, No. 52.

¹⁴ W. H. Harrison and P. A. Subramania Aiyer, *Mem. Dept. Agric. India, Chem. Ser.*, 1914, **4**, 1; *A.*, i, 202.

taining bacteria which oxidise hydrogen and methane and produce carbon dioxide, which is assimilated by algæ with liberation of oxygen. The activity of the film bacteria is increased by green manure, and this gives rise to an increased production of oxygen. The oxygen dissolved in the water entering the soil is, however, one of the chief factors on which the crop depends

An investigation on the production of nitrates in the black soils of the arid regions in Russia, extending over several years, showed that, under favourable conditions of tilth and temperature, nitrification may be very active, and nitrates may accumulate in considerable amounts.¹⁵ Comparing the different fallows, to which reference has been made in connexion with aeration, it is shown that the greatest amount of nitrates is produced on the "black" fallows and the April fallows, the greatest accumulation being found towards the beginning of August. The sooner the fallow is ploughed in spring the greater the accumulation of nitrates. The depth to which cultivated land is ploughed seems to have no great influence.

In plots with winter cereals, the nitrates diminished rapidly, being, to a great extent, taken up by the crop. When the soil is broken up after the harvest of winter cereals, nitrates may be formed in considerable amounts by the end of September provided that the weather is favourable. The results accord with the results of crop experiments on the different fallows, and they indicate that aeration is of greater importance than temperature.

On these soils, applications of dung result in only slightly increased production of nitrates.

Humus.

Whilst a good deal of progress has been made in recent years in our knowledge of the various definite organic compounds which occur in soils, it cannot be said that recent investigations on humus have resulted in any very material advance. The papers published in 1915 deal mainly, not with soil humus, but with the substances obtained by the action of acids on carbohydrates and proteins.

When zein and tryptophan are hydrolysed separately, no intensely black solution is obtained.¹⁶ With a mixture of the two substances there is, however, a rapid development of an intense blackness, and the addition of dextrose to tryptophan enables about 90 per cent. of the nitrogen of the tryptophan to be re-

¹⁵ N. M. Toulakoff, *Bull. Agric. Intell. Plant Diseases*, 1915, **6**, 797.

¹⁶ R. A. Gortner and M. J. Blish, *J. Amer. Chem. Soc.*, 1915, **37**, 1630; *A.*, i, 726.

covered as humin. No humin was obtained from a mixture of histidine and a carbohydrate.

As carbohydrates yield small amounts of furfuraldehyde when boiled with mineral acids, it is suggested that in the production of humin the reaction involved is a condensation of tryptophan with an aldehyde.

The artificial humic acids hitherto obtained from sugar by the action of acid contain more carbon than humic acid from soil. It has been found, however, that when natural humic acid is extracted with absolute alcohol, the product has the same composition as humic acid from sugar.¹⁷ It is not clear what became of the nitrogen of the humic acid obtained from peat.

By boiling mucin and egg-albumin with hydrochloric acid for eight hours, 2 to 3·5 per cent. of humic acid was obtained. Caseinogen and purified egg-albumin, on the other hand, yielded practically no humic acid when subjected to the same treatment.

In order to throw some light on the value of soluble humus as a food for plants, pot experiments have been made in which four successive crops—wheat, mustard, rye, and mustard—were grown in garden and arable soils, and in the same soils after removing nearly all the soluble humus by extracting with 2 per cent. sodium hydroxide.¹⁸ The first crop gave better yields, and took up more nitrogen in the extracted soil than in the original soil; and in five out of eight cases the extracted soils parted with rather more nitrogen than the unextracted soils. By combining all the results obtained with the four crops in each case, it is shown that the plants obtained slightly more nitrogen from the extracted garden soil than from the original soil, whilst with the arable soil the results were reversed. The differences are, however, very slight, not only as between extracted and unextracted soils, but also between the garden and arable soil. The total nitrogen removed from the untreated garden soil, which contained 0·315 per cent. of nitrogen, amounted to 1·07 gram, whilst the extracted arable soil, containing 0·109 per cent. of nitrogen, parted with just the same amount. Expressed as percentages of the amount of nitrogen actually present, the four crops assimilated about 7 per cent. of the nitrogen (soluble and insoluble) present in the garden soil and about 20 per cent. of the insoluble nitrogen remaining in the extracted arable soil.

It was further shown that the extraction of humus, which of course involves an initial treatment with dilute acid as well as

¹⁷ W. B. Bottomley, *Bull. Agric. Intell. Plant Diseases*, 1915, **6**, 1162; *Biochem. J.*, 1915, **9**, 260.

¹⁸ W. Weir, *J. Agric. Sci.*, 1915, **7**, 246.

extraction with alkali, produced changes which are observed in partial sterilisation with antiseptics—a fall in the number of bacteria followed by a great increase, increased ammonia production, and diminished nitrification.

Unless the treatment of the extracted soils introduced some lasting stimulating effect to compensate for the loss of directly available nitrogen, the results seem to indicate that insoluble humus is broken down a good deal more rapidly than has been supposed. It would be desirable to prolong an experiment of this kind, and to ascertain by subsequent extractions, at suitable intervals, the rate at which soluble humus is produced. Since about 40 per cent. of the total soil nitrogen is extracted by alkali, and about 20 per cent. of the rest can be removed by four crops, it should not take long to reach the point when nitrogen hunger becomes evident.

Tetracarbonimide has been obtained from soils in Florida, Virginia, Maryland, and Washington, D.C., in quantities sufficient for purification and identification, and it is estimated that a hectare of soil to a depth of 30 cm. contains about 8 kilos. of this substance.¹⁹ As uric acid is not known to occur in soils or plants, it seems likely that the tetracarbonimide found in soils is derived from purine bases. Xanthine, hypoxanthine, and adenine all occur in soils, and guanine has been found in a heated soil.

Partial Sterilisation of Soils.

Further experiments on the partial sterilisation of soils showed that with any particular antiseptic no increase in the amount employed over the amount required to produce the usual partial sterilisation had any further effect.²⁰ Paraffin hydrocarbons give rise to a depression in the number of bacteria and a decided increase in the ammonia, without, however, suppressing the nitrifying organisms and the protozoa. Results similar to these, although less marked, are obtained by merely air-drying the soils in thin layers for twenty-four hours. Substances which are not completely removable from the soil leave a lasting effect on the flora. With lower concentrations two or three species of bacteria, according to the substance employed, multiplied temporarily to an enormous extent, without, however, increasing ammonia or nitrite production.

Whilst volatile antiseptics are undoubtedly effective in increasing the productiveness of a soil under pot-culture conditions, they

¹⁹ E. C. Shorey and E. H. Walters, *J. Agric. Research*, 1914, 3, 175; *A.*, i, 1092.

²⁰ W. Buddin, *J. Agric. Sci.*, 1914, 6, 452; *A.*, i, 112.

are unsuitable for application on a large scale. For that purpose a solid substance is desirable.

Some experiments with frozen soils showed a decided increase in the number of bacteria.²¹ The results are difficult to account for, but it is suggested that if the change is due to the same causes which give rise to the increase in soils partly sterilised by heat or antiseptics, a cold winter may be expected to be more beneficial to crops than a warm one.

Further results of an investigation on the employment of lime²² for the partial sterilisation of soils, to which reference was made last year, showed that whilst the amount of lime required by different soils may vary considerably, and that both a deficiency and an excess are to be avoided, it is not a difficult matter to ascertain by laboratory experiments the approximate amount of lime which should be applied to obtain the desired results. For this purpose samples of the soil (100 grams) are treated with calcium oxide in quantities of 0.1 to 1 gram and 50 c.c. of water, shaken at intervals for a few hours, filtered, and washed with a further 200 c.c. of water. The amount of lime which gives a filtrate, the whole of which requires 5—10 c.c. of *N*/10-acid for neutralisation, may be taken as the limit to which lime must be applied. The amounts of lime required to produce an alkaline reaction agree closely with the amounts which produce the characteristic partial sterilisation effects as indicated by the destruction of protozoa and the inhibition of nitrifying organisms. The results of pot experiments showed that the amounts of lime as indicated by the above method coincide with the amounts required for the maximum production of dry matter and also the maximum production of dry matter in the first four crops. Larger amounts of lime increased the production of ammonia and nitrates, but not the crop.

The results of experiments on the relation of protozoa to bacteria are conflicting. On the one hand, it has been shown that addition of protozoa to an ammonifying solution resulted in a decided limiting effect on the number of bacteria, whilst some evidence, not absolutely conclusive, was obtained that the protozoa had an inhibiting effect on the production of ammonia. In soil experiments it was found that by inoculating sterilised soil with protozoa and bacteria, and with bacteria alone, there was a marked reduction in the bacterial numbers when protozoa were present.^{22a}

Other experiments have indicated that the presence of 10,000 protozoa per gram of soil failed to reduce the bacterial content

²¹ H. J. Conn, *New York Agric. Exper. Stat. Techn. Bull.*, 35.

²² H. B. Hutchinson and K. McLennan, *loc. cit.*

^{22a} A. Cunningham, *J. Agric. Sci.*, 1915, 7, 49.

of a soil to the level of a soil containing no protozoa kept under conditions favourable to the trophic existence of amœbæ and flagellates.²³ It was not found possible by inoculation with protozoa to restore to soils which had been partly sterilised the factor which limits bacterial activity, and from these results the conclusion is drawn that the limiting factor is not of protozoan origin.

In reference to the last results it has been pointed out that by inoculating partly sterilised soils with hay infusion the normal soil fauna is not added, and that the addition of protozoa to a partly sterilised soil, somewhat changed in the process, does not make it correspond exactly with the original untreated soil.²⁴

In accordance with previous observations, it has again been shown that by heating soils the solubility of some constituents is increased.²⁵ Extracts of heated soils showed an increasing depth of colour with each rise in temperature and an increase in conductivity; whilst in the case of soils heated to higher temperatures the extracts showed an increased depression of freezing point, about half of which is due to electrolytes. Another effect of heating was a change in the texture of the soil, resulting in an increased power of retaining water.

Soil Bacteriology.

The examination of a large number of soils showed that *Azotobacter* is less widely distributed than is generally supposed, and that it is not always found in soils containing sufficient amounts of basic substances, although the basic character of the soil is the main factor on which its presence depends.²⁶ It occurs very commonly in soils which contain sufficient calcium carbonate to effervesce when acid is added, but is rarely found in neutral soils, and scarcely ever in acid soils, and its disappearance from a soil is usually caused by the absence of basic substances, especially calcium and magnesium carbonates, and not by the presence of a toxic substance. As regards phosphoric acid, indications were obtained that when a mannitol solution free from phosphates produces a vigorous growth of *Azotobacter* after inoculating with a soil, it may be assumed that the soil is not deficient in phosphoric acid.

In the soils of Danish forests *Azotobacter* was found in only two out of sixty-four localities, and both the soils which gave positive

²³ T. Goodey, *Proc. Roy. Soc.*, 1915, [B], 88, 437.

²⁴ E. J. Russell, *ibid.*, [B], 89, 76.

²⁵ A. Wilson, *Sci. Proc. Roy. Dublin Soc.*, 1915, 14, 513; *A.*, i, 1090.

²⁶ H. R. Christensen, *Centr. Bakt. Par.*, 1915, ii, 43, 1; *A.*, i, 196.

results were from beech woods and contained carbonates.²⁷ The organism, which was not the usual form, but probably *A. Beijerinckii* or *A. vitreum*, was also found in a black peat which effervesced with acid. The forest soils rarely contained enough carbonate to effervesce, but were frequently neutral or slightly alkaline. They contained, however, calcium in other forms.

It is considered probable that the absence of *Azotobacter* may be due partly to the low temperature, a deficiency of calcium carbonate, and an excessive amount of humus. The nitrogen supply of the soils would seem to be obtained by some other organism.

The results of weekly inoculation experiments with Pusa soils showed that the fixation of nitrogen is most active from June to September, which is the rainy season with fairly high temperature; whilst the lowest results were obtained from October to January, being coincident with the drying of the soil and lower temperatures.²⁸

As regards the amounts of water most favourable to nitrogen-fixation, it has been found in experiments with a light sandy soil kept at a temperature of 28—30° that the greatest amounts of nitrogen were fixed when the soil contained 20—24 per cent. of water. The former amount corresponds with the optimum as indicated by physical tests.²⁹

Experiments have been made on the fixation of nitrogen in culture solutions by *Azotobacter* in the presence of various organic compounds, both non-nitrogenous and nitrogenous.³⁰ On the whole, the substances employed had not much effect, and the action was generally different from what has been observed with plants. Of the different non-nitrogenous compounds employed, quinol and salicylaldehyde were found to be the most toxic, whilst esculin, quinic acid, and borneol acted as stimulants. As regards nitrogen compounds, nicotine, picoline, guanidine carbonate, and scatole all showed the toxic properties usually ascribed to them; caffeine seemed to stimulate growth. Several compounds, especially the simpler ones, such as carbamide, glycine, formamide, and allantoin, had a depressing effect on nitrogen-fixation, possibly owing to the substances being assimilated in preference to elementary nitrogen.

In order to ascertain to what extent *Azotobacter* is able to

²⁷ F. Weis and C. H. Bornebusch, *Bull. Agric. Intell. Plant Diseases*, 1915, 6, 546; *Det forstl. Forsøgsvæse i Danmark*, 4, 319.

²⁸ J. H. Walton, *Mem. Dept. Agric. India, Bact. Ser.*, 1915, 1, 97; *A.*, i, 1039.

²⁹ C. B. Lipman and L. T. Sharp, *Bull. Agric. Intell. Plant Diseases*, 1915, 6, 1167; *Bot. Gaz.*, 1915, 59, 402.

³⁰ H. S. Reed and B. Williams, *Centr. Bakt. Par.*, 1915, ii, 43, 166; *A.*, i, 196.

utilise humus and the non-nitrogenous compounds which occur in soils, experiments have been made on the behaviour of the organism towards humates and a number of sugars, alcohols, acids, and other substances.³¹

As regards humates, it was found that the potassium and calcium salts are not utilised in absence of additional combined nitrogen, and that whilst there was growth when ammonium humate was supplied, no nitrogen was fixed. With polysaccharides, especially gum tragacanth and inulin, with arabinose, xylose, lævulose, and some other sugars, nitrogen fixation was vigorous; with lactose less nitrogen was fixed. Of the different alcohols employed, ethylene glycol gave the highest results, and then mannitol; whilst with methyl, ethyl, and propyl alcohols the amounts of nitrogen fixed per gram were respectively 2.1, 4.0, and 9.2 milligrams. Good results were obtained with some of the acids (as calcium salts), especially lactic acid; succinic acid came next, whilst with maleic and glycollic acids only small amounts of nitrogen were fixed, and with meconic acid none at all. Fatty acids were found to be readily utilised, the amount of nitrogen fixed rising with the increase in molecular weight from 1.47 milligrams with formic acid to 6.08 milligrams with butyric acid. Most of the naturally occurring glucosides, and all the benzene derivatives employed, were found to be unsuitable as sources of energy for *Azotobacter*.

In the case of the four fatty acids it is shown that the ratios of nitrogen fixed to the heat of combustion are almost constant, and that the same holds good in the case of starch, dextrin, and gum arabic, allowing for experimental error, which is greater with these substances than with the simpler compounds. This close relation is not, however, general, and no regularity is observed with the series of monohydric alcohols.

Whilst the failure of potassium and calcium humates to support the life of *Azotobacter*, if confirmed, seems rather remarkable, although practically not of much importance, since some of the products of the decomposition of humates would probably be available, the results on the whole indicate that in normal soils suitable food of some kind may generally be expected to be present in sufficient amounts.

The absence of antagonism between calcium and magnesium chlorides for *B. subtilis*, as an ammonifying organism,³² has been explained on the assumption that calcium is not essential for bacteria as it is for chlorophyllous plants.³³ It is now shown that this explanation is inadequate, since it has been found that in the

³¹ F. A. Mockeridge, *Biochem. J.*, 1915, **9**, 272; *A.*, i, 754.

³² C. B. Lipman, *Bot. Gaz.*, **49**, 41.

³³ O. Loew, *ibid.*, 304.

case of *Azotobacter chroococcum* calcium carbonate overcame the toxic effect of magnesium carbonate.³⁴

In water cultures, calcium carbonate was found to act as a stimulant towards *Azotobacter* in concentrations up to 2 per cent., whilst magnesium carbonate is toxic in concentrations of not more than 0.1 to 0.2 per cent. Addition of calcium carbonate to cultures containing 0.2 per cent. of magnesium carbonate became effective when the amount reached 0.75 per cent., and the maximum antagonistic effect was obtained with 1.25 per cent.

In soil cultures (a sandy soil was employed), calcium carbonate alone had no effect up to 1.4 per cent. of the dry matter of the soil, and larger amounts were toxic. Magnesium carbonate proved to be more toxic in soil than in solutions, nitrogen fixation being almost completely inhibited by 0.1 per cent. With this amount of magnesium carbonate, addition of calcium carbonate has a protective action, the best results being obtained when the ratio $\text{CaCO}_3:\text{MgCO}_3$ was about 15:1.

The toxic action on *Azotobacter* of calcium carbonate when soils contain more than 1.5 per cent. is of considerable interest, although it seems likely that the amounts which are toxic will vary with different types of soil, and in some cases may be a good deal higher than in the case of the sandy soil employed in these experiments. The results seem clearly to indicate the desirability, in the case of soils which require calcium carbonate, of ascertaining how much is actually required, so as to avoid a large excess. If soils in which *Azotobacter* may be assumed to be active do not, as time goes on, become more nitrogenous, they would, no doubt, become poorer in nitrogen if the activities of the microbe are in any way checked.

As the toxic effect of magnesium carbonate has been attributed to its alkalinity, it should be mentioned that the alkalinity was found to be favourable rather than otherwise.

Certain compounds of arsenic have been found to stimulate the fixation of nitrogen by *Azotobacter*.³⁵ Of the different substances employed, lead arsenate gave the best results, and it was also found to be the least toxic, as much as 400 parts per million being harmless. Paris green, which is very toxic, even when only 120 parts per million are present, failed to produce stimulation in any concentration. The results resemble those previously obtained in nitrification experiments. The stimulation of *Azotobacter* by arsenic is greatest when the water-soluble arsenic amounts to about 10 parts per million. In the case of soils containing plenty of

³⁴ C. B. Lipman and P. S. Burgess, *J. Agric. Sci.*, 1914, **6**, 484; *A.*, i, 72.

³⁵ J. E. Greaves and H. P. Anderson, *Centr. Bakt. Par.*, 1914, ii, **42**, 244; *A.*, i, 484.

organic matter, addition of arsenic resulted in as great an increase in the amount of nitrogen assimilated as when mannitol was added without arsenic.

Only one type of *Azotobacter* was isolated which was stimulated by arsenic. The stimulation is attributed to the organism being enabled to utilise more economically its source of carbon. In soils, the favourable effect of arsenic is considered to be partly due to the destruction of undesirable species. A number of soils were employed in these experiments, differing widely both physically and chemically.

A study of the influence of phosphates and sulphates on ammonification in peptone solutions, with both pure and mixed cultures, showed that potassium dihydrogen phosphate greatly increased the production of ammonia, especially at the end of the first two days. Bone-ash had no effect, whilst calcium and potassium sulphates slightly increased ammonification.³⁶ The increased production of ammonia in the presence of potassium dihydrogen phosphate is not due to increased efficiency, but to an enormous increase in the numbers of the bacteria.

In soils it was found that potassium dihydrogen phosphate caused a distinct gain in ammonification, and that tricalcium phosphate also stimulated ammonification by increasing the multiplication of the bacteria. Calcium, magnesium, and potassium sulphates also had stimulating effects.

All these compounds, especially the phosphates, increased the production of carbon dioxide. It would seem, therefore, that apart from their direct manurial value, the manures act indirectly in increasing the supply of available nitrogen, and also the supply of available minerals as a result of increased amounts of carbon dioxide.

A new nitrite organism has been isolated from Pusa soil³⁷ which is stimulated by an atmosphere containing 50 per cent. of carbon dioxide, whilst further amounts have a retarding effect. In the presence of phosphates, the organism produces nitrites from ammonium salts, asparagine, and carbamide; when, however, phosphates are absent, only ammonium carbonate is readily converted into nitrite. Calcium carbonate, which is more suitable than magnesium carbonate for providing a base, seems to have an inhibiting effect in the case of ammonium carbonate and carbamide. The action of the organism is inhibited by 0.4 per cent. of dextrose in Omelianski's solution, and retarded by 0.4 per cent. of asparagine.

³⁶ E. B. Fred and E. B. Hart, *Wisconsin Agric. Exper. Stat. Research Bull.*, 35, 1915; *A.*, 1916, i, 104.

³⁷ N. V. Joshi, *Mem. Dept. Agric. India Bact. Ser.*, 1915, 1, 85; *A.*, 1916, i, 105.

Experiments with a number of soils showed that their power of decomposing peptone varies very considerably, and depends both on chemical conditions, in which phosphoric acid has an important share, as well as on biological factors.³⁸ Application of calcium carbonate was generally without effect, and none of the soils was influenced by addition of humus. It was found that, as a rule, a low power of decomposing peptone was coincident with conditions unfavourable to the growth of plants.

The decomposition of cellulose was not affected by inoculation alone, and depends on chemical composition, lime and phosphoric acid being important factors.

The conversion of sulphides in soils into sulphates is shown to be due mainly to bacterial action, although small amounts of sulphide may be oxidised chemically.³⁹ Free sulphur is converted into sulphates much less readily than sodium, potassium, and calcium sulphides. The optimum amount of water in the soil for sulphification is 50 per cent. of the amount required for saturation. Aeration has an important influence, and it is found that addition of sand to soil in gradually increasing amounts results in a corresponding increase in sulphates until 50 per cent. is added; further addition of sand, up to 90 per cent., gradually diminished the production of sulphates, owing to deficiencies of humus and mineral nutrients. The effect of organic matter on the production of sulphates depends on the nature of the substance employed. Carbohydrates, such as sucrose, starch, and cellulose, had a depressing effect, and applications of very large amounts of horse and cow manures and clover hay resulted in a considerable reduction in the amounts of sulphates produced, and, coincidentally, a similar depression in the growth of timothy in a duplicate series. This was followed by an increased production of sulphates and also an increase in the crop. Addition of calcium sulphate to the soil was found to have a very marked stimulating effect on the conversion of sulphides and sulphur into sulphates.

The sulphur compounds present in organic manures seem to be converted into sulphates very rapidly.

In the production of sulphates from iron sulphide in soil,⁴⁰ it is stated that the iron alone is first oxidised, and that the sulphur thus liberated is subsequently converted into sulphate.

A number of organisms have been obtained from soils and dust, etc., which have the power of utilising benzene derivatives as the

³⁸ H. R. Christensen, *loc. cit.*

³⁹ P. E. Brown and E. H. Kellogg, *Iowa Agric. Exper. Stat. Research Bull.*, 18, Dec., 1914; *Centr. Bakt. Par.*, 1915, ii, 43, 552; *A.*, i, 763.

⁴⁰ H. Kappen and E. Quensell, *Landw. Versuchs-Stat.*, 1915, 86, 1; *A.*, i, 203.

only sources of carbon.⁴¹ Phenol and phloroglucinol, for instance, are oxidised to carbon dioxide, benzene to fatty acids and carbon dioxide. Catechol is oxidised, probably to hydroxyquinol, and toluene, xylene, and guaiacol were also decomposed. Resorcinol, pyrogallol, tannin, aniline, naphthalene, and anthracene were not decomposed.

Plant Nutrition and Manures.

Although it seems fairly evident that the elementary nitrogen acquired by leguminous and other plants having root-nodules must be fixed initially in the root-nodules, and not in the leaves as has been suggested, the few experiments made in this connexion have not been very convincing. The question has now been settled in a satisfactory manner⁴² by experiments with soja-beans and cow-peas which were grown in Woulfe's bottles through which a mixture of oxygen and carbon dioxide and air respectively were passed; the stems and leaves of the plants were exposed to the air. The results showed that almost no nitrogen was fixed except when nitrogen had access to the roots. Some slight gains of nitrogen were obtained in the case of the plants grown with oxygen and carbon dioxide which are attributed to air dissolved in the water of the gas-holders. In an ordinary atmosphere the plants produced large amounts of roots and root-nodules, whilst without nitrogen the development of roots and root-nodules was very restricted.

Incidentally, the results indicate the importance of aeration when leguminous crops are grown.

Bacteria belonging to the *Bacillus radiculicola* group have been found in the root-nodules of *Ceanothus americanus* growing wild in North America.⁴³ The microbes obtained both from *C. americanus* and *C. velutinus* were found to fix nitrogen in amounts similar to those obtained with the bacteria from *Alnus* and *Elæagnus* nodules.

In the root-nodules of the Cycadaceæ, both *Bacillus radiculicola* and *Azotobacter* have been found.⁴⁴

It has been found in water-culture experiments with rye and barley that, within fairly wide limits, the concentration of the nutrient solution is not very important provided that the solution is frequently changed.⁴⁵ When the solution is not changed, there is a marked depression in the rate of growth, probably due to the

⁴¹ R. Wagner, *Bied. Zentr.*, 1915, **44**, 212; *A.*, i, 628.

⁴² A. L. Whiting, *Univ. Illinois Agric. Exper. Stat. Bull.*, 179, 1915.

⁴³ W. B. Bottomley, *Ann. Bot.*, 1915, **29**, 605.

⁴⁴ E. R. Spratt, *ibid.*, 619.

⁴⁵ W. Stiles, *Bull. Agric. Intell. Plant Diseases*, 1915, **6**, 563.

absorption of the different ions at different rates, resulting after a time in a change in the relative proportions of the different substances.

The weakest solution employed in these experiments contained about the same amounts of potassium and phosphoric acid as were calculated by Cameron to be present in the soil solution, so that it may be considered to be probable that the concentration of the soil solution, although low, is sufficient to produce healthy, if not very large, plants.

On the assumption that the tricalcium phosphate of rock phosphates is rendered available by the action of carbon dioxide and water, dicalcium phosphate and calcium hydrogen carbonate being formed, the amount of soluble phosphate obtained will depend on the amount of calcium hydrogen carbonate which is removed by the plant or in other ways.⁴⁶ From this it seems to follow that plants which contain relatively large amounts of calcium have a relatively high feeding power for the phosphoric acid of crude phosphates, and vice versâ. Peas, beans, clover, lucerne, and cruciferous plants contain relatively high amounts of calcium, whilst in maize, oats, rye, wheat, and millet the amounts are relatively low. According to this theory, it should be possible to ascertain by analyses of the ash of a plant whether a soluble phosphatic manure is required. Other factors have, of course, to be considered. The employment of ammonium salts, for instance, will increase the solubility of the rock phosphate by assisting in the removal of the calcium hydrogen carbonate.

In its general application to insoluble plant foods, the theory would be that the assimilating power of a plant for insoluble substances depends, first, on the solubility of the substance in water and carbon dioxide, and next on the removal by the plant of all the products of the reaction in the proper proportion, so that the reaction can continue indefinitely.

The injurious effect of vanillin on plants has been shown to vary with different soils.⁴⁷ In experiments with clover, an application of 100 parts of vanillin per million, which was gradually raised to 300 parts per million, resulted in a reduction of 53 per cent. in the yield; the plants, however, remained healthy in appearance. In the case of wheat, it was found that vanillin has injurious effects in an infertile sand and in an unproductive sandy loam, whilst the plants grown in a productive loam were not injured by as much as 500 parts per million, the vanillin no doubt being oxidised. In plot experiments, applications of vanillin at the

⁴⁶ E. Truog, *Science*, 1915, **41**, 616.

⁴⁷ J. J. Skinner, *U.S. Dept Agric. Bull.*, 164, 1915; *A.*, 1916, i, 111.

rate of 320 kilos. per hectare to cow-peas, peas, and beans resulted in stunted growth, although the plants slowly matured and were harvested.

Under favourable conditions, vanillin may remain a considerable time in the soil. In the case of a heavy, silty clay loam, for instance, injurious effects were observed six months after vanillin had been applied.

In another series of experiments in which the effects of organic substances on the growth of wheat in water-cultures and in soil were compared,⁴⁸ it was found that whilst 500 parts per million was fatal to wheat in water-cultures, twice that amount applied to soil failed to have any effect. Salicylaldehyde, which varies in its effects on wheat according to the soil, is not toxic up to concentrations of 500 per million, whilst *p*-benzoquinone is beneficial in concentrations below that amount, and coumarin and dihydroxystearic acid are slightly injurious. In water-cultures all these substances have a pronounced toxic action.

An investigation of the effects of vanillin and coumarin⁴⁹ on wheat in water-cultures, in sand-cultures, and in soil showed that both quartz sand and soil have ameliorating effects on the action of vanillin, whilst coumarin has the same effects in sand as in water-cultures; addition of a small amount of soil to water-cultures completely destroyed the toxic action of coumarin, but had no effect in the case of vanillin. From these results the conclusion is drawn that vanillin is only toxic when present in a solution which completely envelops the roots in a continuous layer. In the case of coumarin, the effects of additions of soil in amounts too small for the adsorption of the relatively large amounts of toxin is attributed to the oxidation of the coumarin.

The healthy appearance of the plants which received the highest amounts of vanillin and coumarin, and the absence of inhibiting effects on the growth of the roots, seem to indicate that the depressed yields of wheat were not due to toxicity at all, and that they may be attributed to the general effects of soluble, non-nutrient organic matter, which may affect the micro-flora of the soil, and to some extent the physical conditions of the soil, by forming protective films, or it may interfere with the absorption of certain nutrients by plants. From this point of view vanillin and coumarin, and presumably some other toxins, have no direct action on plants, but influence growth by influencing certain soil conditions.

The results of these experiments make it evident that it is rash

⁴⁸ F. W. Upson and A. R. Powell, *J. Ind. Eng. Chem.*, 1915, **7**, 420; *A.*, i, 635.

⁴⁹ J. Davidson, *J. Amer. Soc. Agron.*, 1915, **7**, 146, 221.

to draw conclusions from water-culture experiments as to what may occur in field experiments. In view of the difficulty of explaining the effects of definite substances which can be taken from one soil and added to another, it seems undesirable definitely to attribute injurious effects to toxins which have not been seen and possibly do not exist.

A number of experiments have been made on the action of radium on germination and growth of plants.⁵⁰ In the case of pea seedlings which were subjected to the action of emanation from radium bromide contained in sealed tubes, a decided retarding effect was observed; whilst a solution of radium bromide containing 0.001 milligram had no effect. When, however, different plants were grown under bell jars along with radium contained in an ebonite box covered with mica, so that the emanation could diffuse, growth was considerably accelerated. On examining the plants grown with radium, it was found that the cells of the stems were narrow and of greater length than those of the check plants, resembling etiolated plants.

In plot experiments with a considerable number of vegetables applications of extracted radium ore, containing two or three milligrams of radium per ton, at the rate of 28—225 kilos. per hectare, nearly always increased the yields. The quality of potatoes and tomatoes was improved.⁵¹

At Reading the experiments with radium which were commenced last year have been continued, the number of radioactive substances employed being increased from three to nine.⁵² Stimulation was observed in a number of cases, the results with onions being especially favourable.

Positive results have also been obtained with "radioactin," which consists mainly of aluminium silicate and contains a small amount of radium salt and larger amounts of thorium. Application of 0.2 gram to a kilo. of soil increased the yield of oat grain about 18 per cent.⁵³

Applications of radium barium chloride solution and of solid radium barium sulphate at the rate of 0.01—1 milligram of radium per acre failed to produce any regular increase in the yield of maize.⁵⁴

It seems generally to be recognised, although not always, that the employment of radium is not likely to be remunerative. It has

⁵⁰ H. Agulhon and T. Robert, *Ann. Inst. Pasteur*, 1915, **29**, 261; *A.*, i, 925.

⁵¹ H. H. Rusby, *Bull. Agric. Intell. Plant Diseases*, 1915, **6**, 1318.

⁵² *Scottish Farmer*, 1915, **23**, 863.

⁵³ B. Schulze, *Landw. Versuchs-Stat.*, 1915, **87**, 1; *A.*, i, 926.

⁵⁴ C. G. Hopkins and W. H. Sachs, *Science*, 1915, **41**, 732.

been estimated that an acre of soil, to a depth of 12·5 cm., contains about 1 milligram of radium, and that the emanation given off by the soil is fifty to one hundred times as much as the amount given off by the upper 12·5 cm. So that to double the emanation in the soil it would be necessary to apply about 75 milligrams per acre. The amount would, no doubt, vary with different soils; the examination of a number of soils in Minnesota showed that the very fertile soils always contained more radium and thorium emanations than the inferior soils.⁵⁵

A number of experiments have again been made on the effects of vegetation of salts of heavy metals and other compounds not usually employed as manure. In the case of aluminium salts it was found that concentrations of 0·005 per cent. retarded the growth of maize, beans, and other plants, whilst solutions containing only 0·0001 per cent. slightly increased growth.⁵⁶ Other experiments with maize indicated that aluminium is essential to growth.⁵⁷ Fluorine is also stated to be essential for the development of maize.⁵⁸ In experiments with various other plants the action of fluorides, although usually found to increase growth and the production of seed, seemed in a few cases to have a retarding effect.⁵⁹

Experiments have also been made with salts of manganese,⁶⁰ lead, and copper,⁶¹ and with boron and iodine.⁶²

Reference has already been made to the relatively slight effect of sulphates as compared with phosphates on the soil flora. As a sulphur manure, the application of calcium sulphate to a silt loam increased the yield of clover 23 per cent., whilst in the case of rape and radishes the sulphate applied in addition to a complete manure increased the yields by 17 and 9 per cent. respectively.⁶³ The presence of sulphates had a marked effect on root development, especially of red clover and rape, resulting in a more extended feeding area for the plants.

Elementary sulphur was generally found to be injurious, even when plenty of calcium carbonate was added.

By means of a bacterial test it has been found that plant food accessories are present in fresh stable manure, and that the amount

⁵⁵ J. C. Sanderson, *Amer. J. Sci.*, 1915, **39**, 391.

⁵⁶ E. Kratzmann, *Bull. Agric. Intell. Plant Diseases*, 1915, **6**, 403.

⁵⁷ P. Mazé, *Compt. rend.*, 1915, **160**, 211; *A.*, i, 110.

⁵⁸ P. Mazé, *loc. cit.*

⁵⁹ A. Gautier, *Compt. rend.*, 1915, **160**, 194; *A.*, i, 111.

⁶⁰ G. D'Ippolito, *Ann. Chim. Applicata*, 1914, **2**, 342; *A.*, i, 52; B. Schulze, *Landw. Versuchs-Stat.*, 1915, **87**, 1; *A.*, i, 926; G. Masoni, *Staz. sper. agrar. ital.*, 1915, **48**, 822.

⁶¹ J. A. Voelcker, *J. Roy. Agric. Soc.*, 1914, **75**, 306.

⁶² P. Mazé, *loc. cit.*

⁶³ E. B. Hart and W. E. Tottingham, *J. Agric. Research*, 1915, **75**, 232.

increases as the organic matter of the manure decomposes.⁶⁴ The amount even in manure two years old seems, however, to be small as compared with bacterised peat, since half a gram of the latter gave a better result than 10 grams of manure. Plant food accessories were also found in root nodules from bean plants.

As regards the manurial value of bacterised peat a number of experiments have been made at Woburn with barley, peas, mustard, and tomatoes.⁶⁵ The beneficial effect of the peat manure was very marked in the case of mustard, whilst the yields of barley and peas were also increased. In these experiments, which were made in pots, one part of bacterised peat was mixed with eight parts of soil, forming the top 15 cm. This would correspond with an application of about 100,000 kilos. per acre.

Apart from these experiments there does not seem to be very much evidence as to the value, or otherwise, of the peat manure.

Reference was made last year to some experiments on the effects of applying nitrates at different depths. A new series of experiments has been made, in which ammonium sulphate was similarly applied to sugar-beet on a loamy soil.⁶⁶ It was found that the best results were obtained when the manure was dug in to a depth of 10 cm., whilst very satisfactory results were also obtained on the plots dug to 30 cm. When the manure was applied as a top dressing, or was dug in to a depth of only 5 cm. growth was more prolonged and there was a predominance of leaf over root.

The results of estimations of nitrates in the soil at different periods indicated that no loss of nitrate occurred under the conditions of the experiments.

The application of manures in little heaps, with each seed, by means of a special drill, has been found to result in considerably increased yields in grain and straw in the case of wheat manured with superphosphate and with vetches manured with basic slag.⁶⁷

Satisfactory results were also obtained with oats manured with sodium and calcium nitrates, ammonium sulphate, dried blood, potassium chloride, and manganese sulphate respectively; whilst with potassium sulphate and especially with cyanamide the results were unfavourable.

Experiments have been made on the production of nitrates from sewage sludges applied to three different soils.⁶⁸ The sludges con-

⁶⁴ W. B. Bottomley, *Proc. Roy. Soc.*, 1915, [B], 89, 102.

⁶⁵ J. A. Voelcker, *J. Roy. Agric. Soc.*, 1914, 75, 318.

⁶⁶ L. Malpeaux, *La Vie agric. rurale*, 1915, 5, 61; *Bull. Agric. Intell. Plant Diseases*, 1915, 6, 1170.

⁶⁷ L. Brétignière, J. Cartier, and Lévêque, *Ann. École Nat. Agric. Grignon*, 1915, 4, 1; *Bull. Agric. Intell. Plant Diseases*, 1915, 6, 1459.

⁶⁸ C. B. Lipman and P. S. Burgess, *California Agric. Exper. Stat. Bull.*, 251,

tained from 1.23 to 2.66 per cent. of nitrogen. The results showed that the amounts of nitrates produced from the different sludges in the same soil varied considerably, and that variations also occurred with the same sludge in different soils. That is, of course, to be expected.

As compared with other organic manures, such as dried blood, tankage, fish guano, and cottonseed meal, it was found that the nitrogen of the sewage sludge was greatly superior to that of the other manures, being much more readily converted into nitrates.

The results of a number of manurial experiments with sewage sludge made in different parts of England⁶⁹ are not so encouraging as those just referred to. The general results seem to indicate that, under the conditions of the experiments, the nitrogen of the sludge only slowly becomes available; too slowly, in fact, for such crops as potatoes and roots. So that the manure would seem to be best suited to certain pastures and meadows, on which, however, the applications would have to be more limited than on arable soil. Further experiments are evidently needed.

A new method has been devised for the preservation of liquid manure in the pit, which is based on the existence of lactic acid bacteria having the power of preserving fresh urine.⁷⁰ Ten per cent. of a broth made from sugar-beet is mixed with 90 per cent. of water inoculated with *Bacillus cucumeris fermentati*, which is employed for preserving potatoes, and thrown into the manure pit. Instead of sugar-beet, 5 per cent. of molasses or 10 per cent. of a mixture of sweet potatoes can be employed.

The amount of sugar required to preserve 100,000 kilos. of liquid manure is stated to be 500 kilos., corresponding with 3,100 kilos. of sugar-beet. The bottom and walls of the pit should be made water-tight with tar, and it is desirable to add a small amount of oil to exclude air.

N. H. J. MILLER.

⁶⁹ *J. Board Agric.*, 1915, **22**, 235.

⁷⁰ Schmoeger, *Bull. Agric. Intell. Plant Diseases*, 1915, **6**, 1308.

MINERALOGICAL CHEMISTRY.

THE present Report is similar in its scope to last year's account, and is divided fairly equally between the three principal topics: X-ray work, experimental mineralogy, and chemical crystallography. Whilst recognising to the full that such a selection is invidious and possibly unsatisfactory, the writer must point out that a selection has, perforce, now to be made in view of the recent fundamental extension of the old, familiar lines of investigation. The principal deficiency of this and the two previous Reports undoubtedly lies on the side of systematic mineralogy; it is therefore fortunate that this want of completeness is fully compensated by the recent appearance of the third Appendix to Dana's "System of Mineralogy," dealing with the years 1909-1915.

*X-Ray Methods of Exploring Crystal Structure.**

This subject is becoming so important that we may with advantage commence with an epitome of the salient features of the general advance; these are:

(1) The appearance of the book "X-Rays and Crystal Structure," by W. H. and W. L. Bragg, whose brilliant discoveries have been recently recognised by the award of a Nobel Prize. The work is not only welcome as providing a clear and fascinating résumé of what has already been briefly noted in these Reports, but also

* A very full and complete bibliography of papers relating to X-rays since the "Laue-year" 1912 is included in a booklet by I. Malver ("Untersuchungen über die Hochfrequenzspektra der Elemente" (Lund, 1915), who has extended some of Moseley's investigations (compare *Ann. Report*, 1914, 277). It will be remembered that one of the many fundamental, chemical consequences of Moseley's work is that the atomic numbers of cobalt and nickel are in the reverse order of that presented by the atomic weights. On the other hand, it is now found by Malver that in the case of iodine and tellurium the atomic numbers do follow the order of atomic weights, although the latter are just as much at variance with the periodic classification; the wave-lengths of a series of X-rays emitted by iodine are all greater than the corresponding wave-lengths emitted by tellurium.

because it contains a considerable amount of matter not hitherto published.

(2) A marked advance in the theoretical interpretation of the relative intensities of reflection of X -rays at various structural planes. The interpretation has now assumed a quantitative form, involving the atomic masses of the diffracting centres.

(3) The independent elucidation of the structure of the spinel group by different methods. Nishikawa (of Tokyo) employed the apparently cumbersome Laue method, involving a study of X -radiograms, whilst W. H. Bragg's analysis was founded on the results obtained by the X -ray spectrometer. The results were identical. Although, of course, the two methods really depend on the same fundamental behaviour of crystal structure when confronted with X -rays, there can be little doubt that the dual achievement should reassure a general reader, who might otherwise be disposed to wonder whether the rapidity of recent progress may not eventually prove to have been at the cost of permanence.

(4) The measurement by F. Canac¹ of a crystal of sucrose by the X -ray spectrometer instead of the goniometer! The mean result from various measurements can be put in the form $a:b:c = 1.260:1.0.879$; $\beta = 103^\circ 30'$. The accepted values derived from the goniometer are $a:b:c = 1.259:1.0.878$; $\beta = 103^\circ 30'$. Such methods have obviously a great future.

Any exploration of a particular crystal structure, when carried out to that degree of intimacy we have learnt to expect from the researches of W. H. and W. L. Bragg, involves certain problems which (at any rate, in the relatively simple cases so far examined) may be held to be distinct and two in number; first, we have what may be termed the discovery of the grosser aspect of crystal architecture, namely, the discrimination of the Bravais space lattice on which the "structural units" are disposed; secondly, the probing of the much finer details, namely, the dissection of this unit, both with respect to its mass ("molecular weight") and to the relative arrangement of its constituent atoms.

An infinitely extended Bravais space lattice is merely the regular spacial multiplication of a parallelopipedal cell. In crystallography its description is generally given in the form of the ratios $a:b:c$ of its three edge lengths (and the angles α , β , and γ). On the other hand, the spectrometric determination of the various angles, θ , at which any structural plane intensely reflects X -rays, leads immediately to a knowledge of the absolute distance, d , between successive layers of units—for in the fundamental equation $n\lambda = 2d \sin \theta$ the term λ is now known in absolute units, and the term n , express-

¹ *Compt. rend.*, 1914, 159, 405.

ing the order of the reflection (whether first, second, third, or fourth), can generally be determined cursively; if any mistakes were made in n the error would be detected when other structural planes are put to the test of experiment. It will be obvious that the determination of the grating-distances, d_1 , d_2 , d_3 , for three non-tautozonal structural planes of known inclinations, are sufficient to determine the skeleton of the crystal. In certain complicated cases, amongst which may be enumerated the aragonite group, ammonium chloride, sodium chlorate, hæmatite, corundum, quartz, and sulphur, the investigation has not progressed beyond this preliminary stage. Now from the general properties of isomorphous series it can be inferred that the relative distances apart of corresponding structural planes should be substantially in the ratios of the cube roots of the molecular volumes; this expectation has been fully realised by the Braggs in the only cases so far compared, namely, the group sodium chloride, potassium chloride, and bromide, and the members of the calcite group, including sodium nitrate.

The next step is the deduction of the mass associated with the structural unit. The principle employed is best illustrated in terms of a rectangular cell, since its volume assumes the simple form $d_1 d_2 d_3$, say, D . Then the mass associated with the cell is $D\rho$, where ρ is the density of the crystal. Let x be the required fraction of the molecular weight, M the molecular weight, and m the mass of an atom of hydrogen. A little consideration will show that $D\rho = x(Mn)$, whence x may be evaluated. In the case of ammonium chloride x is found to be unity, whilst in potassium chloride x has the value 0.5. This demonstrates that the two substances have fundamentally different structures, a conclusion which was previously deduced by another method.²

In order to solve successfully the riddle of the atomic arrangement account must be taken of the various reflection-intensities. The mean values derived from a considerable number of crystalline substances point to a regular diminution of intensities according to the inverse square law, indicated for the first four orders by the ratios 100:29:7:3.* Now this "normal" fall of intensity is belied by certain structural planes. The abnormalities have received a satisfactory explanation; they are supposed to be due to an inequality of spacing between successive planes (as, for example, in the octahedral planes of diamond) or to a difference in atomic

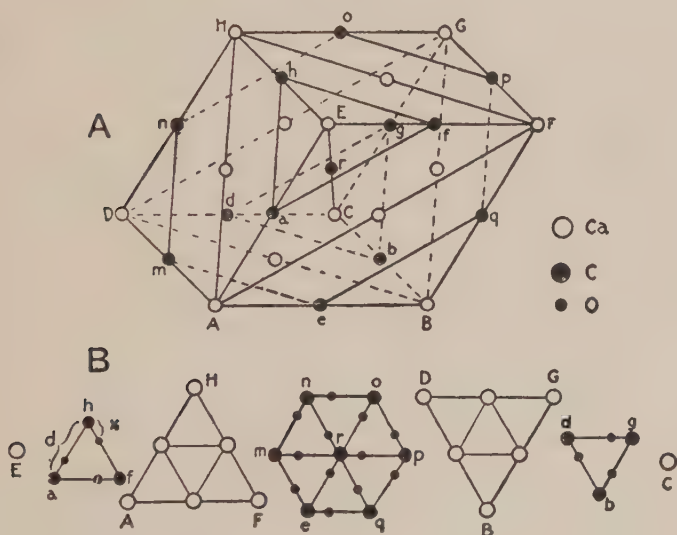
² T. V. Barker, *Min. Mag.*, 1907, **14**, 235; *A.*, 1907, ii, 240.

* The reasons for this diminution are somewhat obscure. W. H. Bragg is disposed to interpret the falling off as due to an inequality in the distribution of the scattering centres (electrons?) throughout the mass of the atom (*Phil Trans.*, 1915, [A], **215**, 266).

composition of these planes (as, for example, in the octahedral planes of sodium chloride) or to both factors combined. It must be noted that the effect of the first factor is purely a matter of geometrical optics; on the other hand, the quantitative treatment of the second factor requires an assumption or hypothesis.

The assumption is, that the reflective power of an atom is a function of its mass. When first made it was in harmony with Barkla's classical work on X-rays,³ and its initial employed in the

FIG. 1.



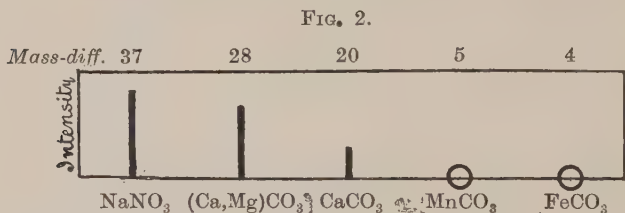
reconstruction of potassium chloride and bromide* and of fluorspar therefore carried a considerable degree of conviction. Further support is forthcoming from the recent work on the calcite group.

The atomic arrangement of the calcite group is indicated by Fig. 1. The upper portion, A, gives a general idea of the position of the calcium and carbon atoms. E is the point of emergence of the principal axis; the three faces of the rhomb represent the

³ Compare G. W. C. Kaye, "X-rays" (1914).

* It may be pointed out that an investigation of rubidium chloride bromide, and iodide should furnish results of much greater weight than can be obtained from any group as yet examined, inasmuch as the atomic weight of bromine is not only almost identical with that of rubidium, but also lies between the atomic weights of chlorine and iodine (also note the great simplicity of the compounds). The series involves, in short, a double *experimentum crucis*.

cleavage planes. The lower portion, *B*, represents successive horizontal layers of *A*, and also includes oxygen atoms. It must be noted that these successive strata have the alternate composition Ca (at. wt. 40) and CO_3 (total wt. 60). The mass-difference of successive layers is therefore 20. The same structure holds for the substances isomorphous with calcite, the full group being NaNO_3 (mass-diff. 37), $(\text{Ca}, \text{Mg})\text{CO}_3$ (28), CaCO_3 (20), MnCO_3 (5), and FeCO_3 (4). Now the fundamental assumption demands that the first order of intensity of reflection from the basal plane should gradually fall with the mass-difference of successive layers, and vanish altogether when the two layers have equal masses. Fig. 2 indicates how closely this expectation is realised; the intensities yielded by manganese and iron carbonate were too small to be registered by the spectrometer.



(energy) of the reflection; the intensity of reflection, then, at any structural plane is given by the square of the mass represented by the chemical composition, for example, 40^2 and 60^2 for the successive basal strata of calcite. A general formula has been derived⁵ which enables the calculation of the theoretical intensities of the first, second, third, and fourth order reflections at any structural plane of an assemblage or reconstruction under examination. The application of this formula to the elucidation of the crystal structures of calcite, sodium chloride, zinc blende, iron pyrites, and magnetite has been attended with great success. In the case of calcite, for example, the ratio $x:d$ of Fig. 1 (*B*), expressing the relative positions of the oxygen and carbon atoms, has now a definite value lying between 0.25 and 0.27, instead of the previously suggested approximation 0.30.

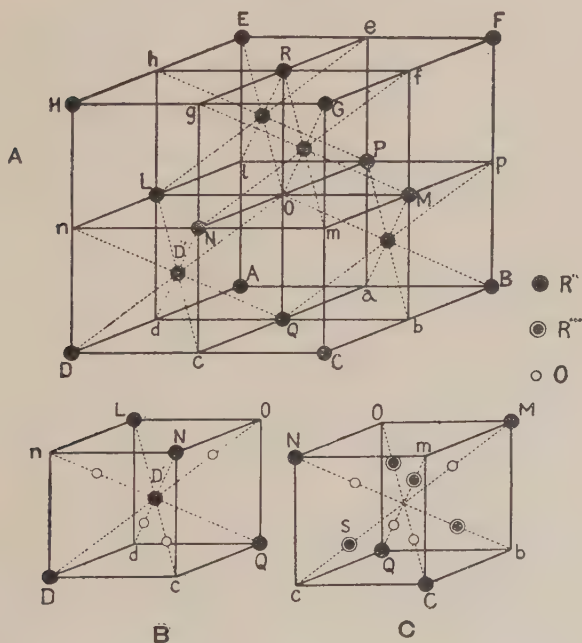
Spinel Group.—This well-known group of minerals, of which magnetite, Fe_3O_4 , and ruby-spinel, MgAl_2O_4 , are prominent mem-

⁴ W. H. Bragg, *Phil. Trans.*, 1915, [A], 215, 266.

⁵ W. H. and W. L. Bragg, "X-rays and Crystal Structure," 121.

bers, has the general formula $R''R_2'''O_4$. For the present kind of work it is necessary to emphasise (as Nishikawa⁶ points out) that whilst oxygen atoms play a relatively insignificant rôle in the *X*-ray behaviour of magnetite, they acquire some importance in spinel owing to the comparatively lower atomic weight of magnesium and aluminium. The method adopted by Nishikawa was to analyse the radiograms obtained by symmetrical and unsymmetrical expo-

FIG. 3.



tures of the crystals, and compare them with the diamond radiograms and structure. By an extremely ingenious train of reasoning a structure was finally obtained which satisfies all requirements. Fig. 3 is a direct reproduction of Nishikawa's diagram. The upper portion (A) is Bragg's diamond structure.* In the spinel group the carbon atoms are replaced by R'' atoms. The positions of the

⁶ S. Nishikawa, *Tokyo Sugaku-Buturigakkwai Kizi*, 1915, [ii], 8, 199.

* A comparison of A with Fig. 3 of last year's Report will betray an unessential difference in the respect that a different group of eight cells was selected. This selection was made advisedly, because it led to a clear diagrammatic appreciation of the chief character of the diamond structure, namely, the tetrahedral environment of every carbon atom.

oxygen atoms are shown in the lower portions, *B* and *C*; the arrangement is seen to be tetrahedral about the centres of both cells. On the other hand, the R''' atoms, being half as numerous as the oxygen atoms, are restricted to that kind of cell, *C*, the centres of which are vacant. The whole assemblage possesses tetragonal screw axes and glide planes of symmetry, and belongs to the class O_h^7 of Schönflies.⁷

The above arrangement is typical of the spinel group as a whole. The individual members differ from each other (1) in the absolute magnitude of the cells, and (2) in the relative positions of the R''' and *O* atoms on the cell diagonals. Consider the diagonal *CO* of Fig. 3 (*C*); for spinel Nishikawa deduces the distance of the oxygen atom from *C* to be 0.36 times the corresponding distance of the aluminium atom, whereas in magnetite the corresponding ratio is something between 0.33 and 0.35. This appears to be the first experimental indication that literally isomorphous crystals (that is, those exhibiting exactly equal angles) possess individual internal characteristics.

The method adopted by W. H. Bragg⁸ was to analyse the various reflections given by the (100), (110), and (111) planes of magnetite. This immediately suggested a structure of the diamond type, the carbon atoms of the latter being replaced by Fe_3O_4 molecules. Considerations of symmetry, the high value of the atomic weight of iron as compared with that of oxygen, and, finally, the calculation of the theoretical intensities, led to the structure independently deduced by Nishikawa. Spinel itself is at present under investigation.

Laue X-Radiograms.—Friedel's theoretical deduction, that the symmetry of a radiogram should be identical with the crystal symmetry to which has been added a centre of symmetry, has derived extensive support from the comprehensive investigations of Haga and Jaeger.⁹ The earlier results of one of these workers, whilst confirming the truth of the Friedel theorem for crystals belonging to the isotropic and uniaxial groups, seemed to disclose a want of agreement in the case of biaxial crystals. Thus the planes (100) and (010) of cordierite, (010) and (100) of sodium ammonium *d*-tartrate, and (010) of hambergite gave radiograms, characterised by a single plane of symmetry, whereas two mutually perpendicular planes are to be expected from the rhombic symmetry of the crystals. Later and more comprehensive researches have to some

⁷ A. Schönflies, "Krystallsysteme und Krystallstruktur" (1891), 548.

⁸ W. H. Bragg, *Phil. Mag.*, 1915, [vi], 30, 305.

⁹ F. M. Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, 17, 1204; H. Haga and F. M. Jaeger, *ibid.*, 430; 1915, 18, 542, 559.

extent explained such anomalies; thus the identical hambergite section previously employed was found to give a normal distribution of spots in certain of its parts and abnormal in other parts. The authors conclude that the unsymmetrical results are referable to a lack of perfect homogeneity [probably the same heterogeneity as has been observed by the Braggs in all crystals of rock salt as compared with crystals of calcite]. The heterogeneity is too delicate to be detected by ordinary optical methods; it must be remembered, however, that the shorter wave-length of X -rays renders them a much finer structural probe. The following exposures are always abnormal: (100) and (010) of cordierite, (100) and (010) of hemimorphite, (010) of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. The remaining pinacoidal exposures of all the rhombic substances and the whole of the exposures obtained with isotropic and uniaxial substances (including basal plane, first and second order prisms), are in agreement with, and substantiate the truth of, the Friedel theorem. Some idea of the indefatigable character of the author's work may be obtained from the following enumeration of the substances investigated, which, it will be observed, represent the majority of the crystal classes concerned:

Cubic.— d - and l -Sodium chlorate; ammonium-iron, and potassium-chromium alums.

Tetragonal.— d - and l -Triethylenediaminecobaltic bromide.

Hexagonal-rhombohedral.—Beryl, apatite, ethyl sulphates of the rare earths; nepheline; calcite; dolomite, phenakite; tourmaline; quartz, cinnabar.

Rhombic.—Aragonite (pseudo-hexagonal), topaz, anhydrite, cordierite, hambergite; hemimorphite, struvite; sodium ammonium d -tartrate, l -asparagine, zinc sulphate (d - or l - not specified, ?).

Another important observation of Jaeger's is that the mineral benitoite, previously supposed by others to exemplify one of the hitherto missing classes of trigonal symmetry, is really optically biaxial; moreover, a "basal" exposure proves the mineral to be merely pseudo-trigonal. The papers are illustrated with a beautiful series of photographic reproductions.

The appearance of the first instalment of a valuable comparison between the results of X -ray work and the theory of the Fedorov-Schönflies generalised point systems may be put on record.¹⁰

The recent advances in our knowledge of crystal structure due to X -ray work has attracted the notice of several mathematical physicists. Attention may be drawn in this connexion to a suite of four papers by Crehore,¹¹ who has derived the equations for the

¹⁰ A. Schönflies, *Zeitsch. Kryst. Min.*, 1915, **54**, 545.

¹¹ A. C. Crehore, *Phil. Mag.*, 1913, [vi], **26**, 25; 1915, **29**, 750; **30**, 257, 613; *A.*, ii, 92.

mechanical forces between atoms and also indicated methods of constructing theoretical molecules and crystals having the properties actually observed. These theoretical investigations already embrace crystals of sodium chloride and diamond, and chemical molecules of hydrogen and the hydrocarbons. The last paper in particular may be recommended to the reader as worthy of perusal, since it contains a description, with diagrams, of mechanically stable molecules of important aliphatic and aromatic hydrocarbons. The work may be regarded as the first serious attempt to lay down a stereochemical theory of precision of the chemist's molecule. Crehore concludes that the essential difference between crystal structure and molecular structure is that atoms in the former, under certain mutual restrictions, may revolve about non-parallel axes, whilst in the latter all atomic rotations are necessarily parallel.

General Conclusions.—Numerous researches have proved that the quality and quantity of the characteristic *X*-rays emitted by an element are independent of its state of chemical combination and valency. Thus it has been shown that the absorption-coefficients of the rays emitted by the following iron compounds are identical: ferrous sulphate, ferric oxide, magnetite, and ammonium ferrocyanide.¹² A little later we had the more quantitative proof that the amount of *X*-rays emitted by a given weight of tin is unchanged after the metal has been converted into the oxide.¹³ Finally, it was shown by Chapman¹⁴ that the characteristic rays of bromine and iodine are emitted by vapours of ethyl bromide and methyl iodide respectively. The scattering of *X*-rays, then, is a purely atomic effect, and it therefore follows that the recent explorations of crystal structure, whilst leading to a knowledge of the mean positions of the various atoms, cannot from the nature of the case throw any direct light on such purely chemical questions as the existence or non-existence of molecules in the crystalline condition.

Thermal Studies of Minerals.

The extremely valuable work published by the American Geophysical school demonstrates how important it is that increased facilities should be offered to such workers as have already shown a real aptitude for research. The work to be reviewed is so extensive that the writer finds it a matter of some difficulty to project its main outlines in true perspective. An idea of its volume may perhaps be gauged from the statement that Rankin and Wright's contribution occupies some seventy pages of tabularly arranged facts

¹² J. L. Glasson, *Proc. Camb. Phil. Soc.*, 1910, **15**, 437; *A.*, 1910, ii, 674.

¹³ J. C. Chapman and E. D. Guest, *ibid.*, 1911, **16**, 136; *A.*, 1911, ii, 568.

¹⁴ J. C. Chapman, *Phil. Mag.*, 1911, [vi], **21**, 446; *A.*, 1911, ii, 357.

and closely reasoned arguments, embodying the results of 1000 experiments and 7000 heat treatments and microscopic examinations. Were it not for the fact that a diagram can often convey much more to the understanding than a corresponding amount of descriptive print, it would be simply impossible to do justice to such comprehensive researches. For a description of the methods employed the reader is referred to last year's Report (pp. 252-255).

*Ternary System, CaO-Al₂O₃-SiO₂.*¹⁵—It may be stated at once that the fourteen substances to be dealt with do not form "solid solutions" to any extent; this feature materially simplifies the problem. Of the three components the melting points of lime and alumina lie at 2570° and 2050° respectively.¹⁶ Cristobalite, the high temperature modification of silica, melts at 1625° or above. The main features of the three binary systems are as follows: The system alumina-silica is quite simple, for the only compound is sillimanite, Al₂SiO₅; its eutectic temperatures with alumina and silica are 1810° and 1610° respectively. It will presently become obvious that the temperature-concentration diagram is presented by the right elevation of the model of Fig. 5. The system lime-alumina is more complicated, since four distinct compounds occur, namely, Ca₃Al₂O₆, Ca₅Al₆O₁₄, CaAl₂O₄, and Ca₃Al₁₀O₁₈. Four compounds require five discontinuities; in the left elevation of Fig. 5 are seen four eutectic dips, and the "alteration point" between CaO and Ca₃Al₂O₆ as a sudden change in the gradient, a little way up the "CaO mountain." The third binary system, lime-silica, also gives rise to four compounds, Ca₃SiO₅, Ca₂SiO₄, Ca₃Si₂O₇, and CaSiO₃; but, inasmuch as the first mentioned does not separate out from the fusion (owing its origin to a combination of CaO and CaSiO₄ when the conglomerate is cooled below 1900°), there are only three "effective" compounds, and consequently four breaks. Three of these breaks (eutectics) are well shown on the back contour of the model, whilst the fourth, an alteration point between Ca₂SiO₄ and Ca₃Si₂O₇, is but faintly indicated.

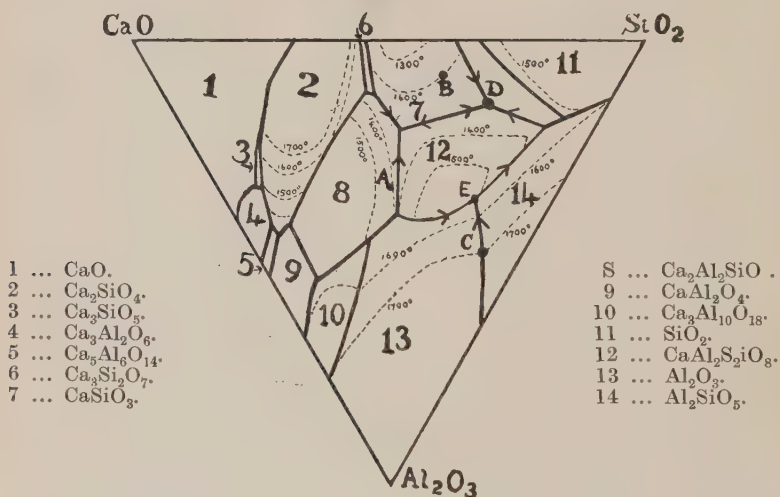
So much for the binary systems. In order to map out the ternary system experiments were made with mixtures of the three compounds representing 5 per cent. intervals of composition. By the application of the methods described in last year's Report it was then possible to determine the nature and composition of the solid phase which is the last to disappear on heating, and also the temperature at which the final trace of solid disappears. Having in this way explored the main outlines of the system, the authors proceeded to the examination of additional mixtures, appropriate

¹⁵ G. A. Rankin and F. E. Wright, *Amer. J. Sci.*, 1915, [iv], 39, 1; A., ii, 50.

¹⁶ C. W. Kanolt, *J. Washington Acad. Sci.*, 1913, 3, 315; A., 1913, ii, 705.

for the final fixing of details. In addition to the three original components and the binary compounds already mentioned, there now appeared three ternary compounds. Two of these, namely, anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (pure gehlenite ?), are stable at their melting points, whereas the third compound, $\text{Ca}_3\text{Al}_2\text{SiO}_8$, is unstable, and has consequently no place in the following stability diagram and space model. The stability diagram (Fig. 4) is constructed on the equilateral principle, generally adopted for systems of three components. Each and every point inside the triangle represents a definite relative concentration of the three components. Thus, the point *A* at the centre of the triangle, being equally distant from the corners, must obviously correspond

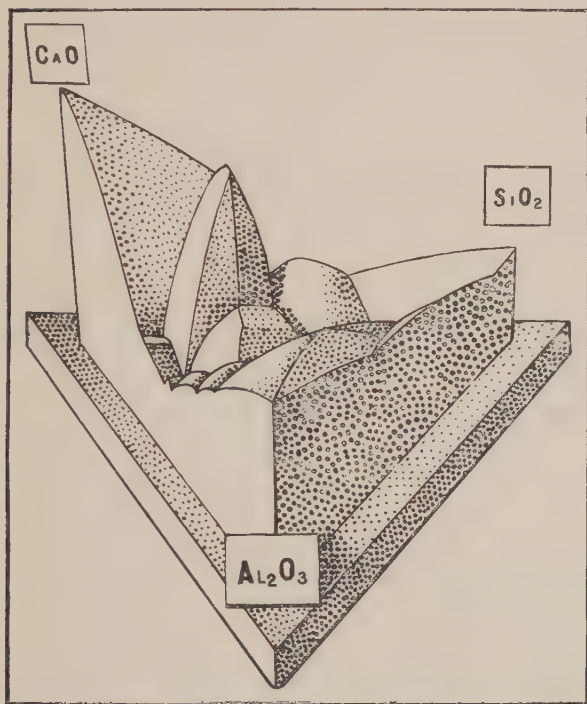
FIG. 4.



with $33\frac{1}{3}$ per cent. each of lime, silica, and alumina. The point *B*, on the other hand, is closest to the silica corner and most remote from the alumina corner; it must therefore correspond with a mixture in which silica preponderates over lime, and lime over alumina. The diagram is divided by thick "boundary curves" into fourteen stability fields, and in this way indicates the particular solid phase which first crystallises from each and every conceivable mixture; thus the mixture *A* deposits the compound $\text{Ca}_2\text{Al}_2\text{SiO}_7$; the mixture *B*, CaSiO_3 (pseudo-wollastonite), and so on. The faintly drawn curves represent a few isotherms. Thus the mixture *B* begins to deposit its pseudo-wollastonite as soon as the fusion is cooled to 1400° ; the mixture *A*, its $\text{Ca}_2\text{Al}_2\text{SiO}_7$, a little above 1400° . Any point on a boundary curve represents a particular mixture,

which on cooling will deposit two solid phases simultaneously; thus the mixture *C* commences to crystallise at 1700° , and forthwith forms a conglomerate of Al_2O_3 and Al_2SiO_5 . The arrows on the boundary curve give the direction of falling temperatures. "Quin-

FIG. 5.



From a photograph of sand model showing relation of binary systems $\text{CaO}-\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3-\text{SiO}_2$ to the ternary system.

tuple points" like *D* and *E*, where three boundary curves meet, represent compositions which on crystallising immediately produce a triple conglomerate of solid phases. *D* is an absolute eutectic, since the temperatures fall towards it along all three curves; on the other hand, the point *E* is a quasi-eutectic, since the curve 12—14 falls away from it.

If it is borne in mind that the isotherms of the diagram (Fig. 4)

are completely analogous to the elevation-contour lines on a topographical map it will become clear that the diagram is really a map of the space model of Fig. 5, in which the vertical dimension represents temperature. The model, of course, gives a far better idea of the variations of temperature through the whole system.

It must now be observed that the diagram, or space model, is incomplete in one important particular, the nature of which can now be described. Consider the fused mixture corresponding in composition with the point *B*, in which silica preponderates over lime, whilst lime greatly preponderates over alumina. When crystallisation sets in, the first phase to separate, namely, CaSiO_3 , has not the composition of the fusion; more especially it contains no alumina. The residual fusion accordingly becomes richer and richer in alumina; its composition is no longer represented by *B*, but by a succession of points, the main trend being an approach towards the alumina corner of the diagram. It must now be stated that an important part of the paper deals with the discussion of the track of this moving point for every conceivable original mixture. It is seen from the diagram that this movement must soon bring *B* to the boundary curve 7-12, and any further cooling must be followed by the appearance of the new phase 12, in the composition of which alumina is represented. Further cooling leads to a movement along the boundary curve 7-12 in the direction of falling temperature, namely, towards *D*. Finally, when the temperature of the residual fusion has attained this point a third phase appears, namely, silica (tridymite), and any further cooling is distinguished by a simultaneous crystallisation of the triple eutectic conglomerate.

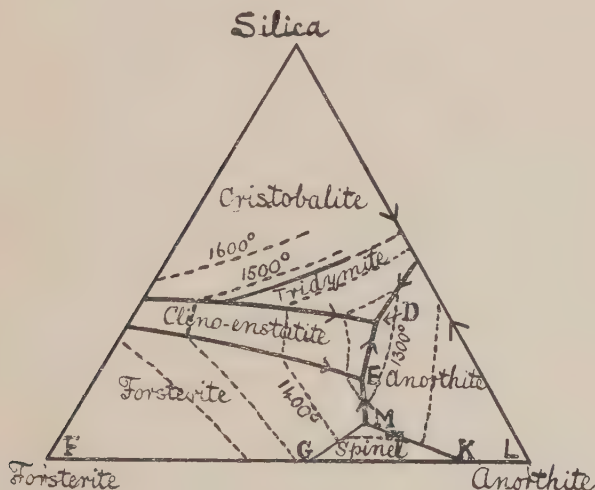
Eutectic crystallisation of alloys is generally characterised by a peculiar interwoven structure—the so-called eutectic structure, which has frequently been invoked to explain certain peculiarities in the texture of rocks. The authors have never been able to detect any trace of this structure in the course of their work.

The above few pages may perhaps convey a general idea as to the scope of a successful and complete investigation of a ternary system of minerals. Such work when prudently interpreted can be made to yield real information as opposed to “opinions” or “speculations” concerning petrological problems. Whilst promising a future discussion of this side of their work, the authors content themselves with pointing out that the prediction they made that the main constituents of portland cement clinker must be the compounds CaSiO_4 , Ca_3SiO_5 , and $\text{Ca}_3\text{Al}_2\text{O}_6$, has been decisively corroborated by the subsequent work of P. H. Bates, of the Bureau of Standards, Pittsburg. Another interesting point of detail is as follows: The constituent Ca_2SiO_4 occurs in three polymorphous

modifications, α , β , and γ , the transformation $\beta \rightarrow \gamma$ being accompanied by a 10 per cent. increase of volume, which shatters the specimen into fine dust. This behaviour is a matter of every-day observation in the burning of portland cement, and is technically known as "dusting."

*System, Anorthite-Forsterite Silica.*¹⁷—Adopting for the time being the fiction that the system is ternary, we may proceed immediately to a consideration of the general diagram (Fig. 6). We see, of course, a division into several fields of stability; a few contour lines (isotherms); two quintuple points, *D* and *E*, having exactly

FIG. 6.



the same significance as in the preceding system. We may also note from the arrows that silica and anorthite form an eutectic (1353°). Since the composition of forsterite is Mg_2SiO_4 , it will be readily appreciated that the binary system, forsterite-silica, is a part of the more general system MgO-SiO_2 , which was described in last year's Report (p. 254). Now the last binary system to be considered is not a little puzzling: mixtures corresponding with points between *F* and *G* deposit forsterite, and mixtures between *K* and *L* anorthite. That is quite regular; mixtures between *G* and *K*, however, do not deposit a possible "molecular compound" forsterite-anorthite, but the mineral spinel, MgAl_2O_4 . There is, then, a chemical reaction between the two supposed components; hence it

¹⁷ O. Andersen, *Amer. J. Sci.*, 1915, [iv], 39, 407; *A.*, ii, 361.

follows that the supposed ternary system cannot be completely explored *per se*; it is an integral part of the quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, the successful working out of which will require years of labour. Although the spinel stability field is represented by the relatively small triangle GKM , the separation of spinel has a direct influence on the larger province FLM . With the exception of this province, the whole of the relationship can be elucidated on the lines of a ternary system, with anorthite, fosterite, and silica as components. Amongst other features of the paper are a very lucid account of the more important types of ternary systems, and a discussion of the petrological significance of the present work, which naturally throws a flood of light on magmatic resorption of olivine and on the hitherto perplexing appearance of spinel in certain rocks.

Effect of Temperature on Crystal Angles.—This subject has been investigated by Rinne¹⁸ within the wide limits of -170° and $+600^\circ$. At -165° the rhombohedral angle of calcite is $74^\circ 44'$, whilst at 596° the angle has increased to $75^\circ 53\frac{1}{2}'$; the value accepted at the ordinary temperature is $74^\circ 55'$ (Wollaston). The variation of the rhombohedral angle with the temperature is not so great in the case of the other carbonates, the order being calcite, rhodochrosite, dolomite, and chalybite. The variation of the angle $(001):(0\bar{1}0)$ for the plagioclase feldspars was also studied, the order of magnitude being albite, labradorite, and anorthite.

Differentiation in Silicate Fusions.

The differentiation of an originally homogeneous liquid magma into chemically distinct layers or sections by processes of diffusion, gravity, convection currents, and the like, has frequently been invoked by petrologists in the interpretation of the complex local problems presented by rocks. It would appear that the operation of gravity in bringing about a sinking of relatively heavy crystals in the fluid magma has lately acquired disfavour, but the experimental work of Bowen¹⁹ serves to establish its truth beyond dispute. The work may be regarded as a petrological extension of the purely physico-chemical research noted in last year's Report. The crucible containing suitable charges of diopside and enstatite was held for different periods of time at a temperature appropriate for a crystallisation of 4 per cent. of forsterite, and then chilled so as to vitreify the remaining 96 per cent. of liquid. A vertical section cut through the mass permitted the microscopical determination of the amount

¹⁸ F. Rinne, *Centr. Min.*, 1914, 705; *A.*, ii, 357.

¹⁹ N. L. Bowen, *Amer. J. Sci.*, 1915, [iv], 39, 175.

of settling of the forsterite crystals due to gravity. The photographic reproductions are conclusive. A similar gravity-differentiation was proved to hold for mixtures which yield pyroxene instead of forsterite. By measuring the velocity of settling and by utilising the results of other researches on mineral, rock, and magma densities,²⁰ the viscosity of the fusion was estimated to be about four hundred times that of water, or, say, about half that of glycerol. When crystallisation of such fusions as first deposit forsterite (olivine) was allowed to complete itself the upper part of the mass was found to consist of pyroxene and free silica, the lower part of pyroxene and olivine—the dissociation of pyroxene into forsterite and silica involved in these experiments was discussed last year. This differentiation occurs in the field in a large scale in the Palisade diabase, described and correctly interpreted by Lewis.²¹

Play of Colours (Aventurisation) in Felspar.

Many gem stones owe their pretty effects to a play of colour brought about by the reflection and interference of light at the upper and lower surfaces of visible, included lamellæ of another mineral. The property is shared by many felspar specimens to a greater or less extent, as in "sunstone" and in "aventurine" varieties respectively. The moonstone and labradorite effects are possibly due to a similar cause; but the lamellæ, if existent, are sub-microscopic.

A notable contribution to the subject of aventurisation has been recently published by Andersen.²² The minerals investigated included albite, oligoclase, and microcline-perthite from various localities. An intelligent use of the two-circle goniometer enabled a very precise determination of the internal structural planes along which the generally platy hæmatite lamellæ are arranged. The colour effect on (001) is chiefly caused by lamellæ along the plane (112) and to a less extent ($1\bar{1}2$), whilst the effect on the surface (010) is always due to lamellæ parallel to the structural planes (150) and ($\bar{1}50$). Less important planes of lamellation are ($\bar{1}13$), ($1\bar{1}0$), (110), ($0\bar{2}1$), (010), and (001). The edges of the lamellæ do not appear to favour any particular orientation. Postulating a refractive index of 3 for hæmatite, Andersen deduced from the polarisation tints a thickness 50—100 $\mu\mu$ for the thinnest and 100—400 $\mu\mu$ for the average lamellæ. The longest lamellæ observed measured 3.5 mm. The platy face of the lamellæ agrees optically with the

²⁰ A. L. Day, R. B. Sosman, and J. C. Hostetter, *Amer. J. Sci.*, 1914, [iv], 37, 1.

²¹ J. V. Lewis, "Annual Rep. State Geologist New Jersey," 1907, 127.

²² O. Andersen, *Amer. J. Sci.*, 1915, [iv], 40, 351.

basal plane of hæmatite. It will be noticed that the structural planes most favoured by the lamellæ are of extremely rare appearance on felspar crystals. This observation may be used as an argument against the view that the hæmatite crystals were deposited on the faces of the growing felspar crystal. Thermal experiments prove that the lamellæ only disappear at a temperature of 1235° , at which incipient fusion of felspar can dissolve hæmatite. The most satisfactory view of the origin of the lamellæ is that they existed in the original felspar in solid solution, and that subsequent cooling led to an unmixing of the hæmatite along certain planes (of gliding or translation?).

Polymorphism.

The need was expressed in last year's Report for a trustworthy method of distinguishing between polymorphous and isomeric (including tautomeric) modifications. An ingenious method has been devised during the year by Sidgwick,²³ depending on the solubility. If to a saturated solution of the more soluble of two polymorphous modifications some of the other modification is added the concentration of the solution will not increase, since the two forms give the same molecule in solution; on the contrary, it will diminish to a greater or less extent, depending on the difference in solubility of the two forms, although this difference may be too small to measure. If, on the other hand, the two forms are isomeric or tautomeric, the addition of the less soluble form will cause an increase in the concentration of the solution, for chemically different molecules do not seriously influence each other's solubility. As a measure of the concentration of the solution, Sidgwick determines the cryohydric point, using an ordinary Beckmann apparatus. The cryohydric points are determined in some suitable solvent for the two forms separately and then for the two forms together. If polymorphous, the mixture of the two forms will give a point lying between those of the separate forms; but if isomeric (or tautomeric) the point given by the mixture will lie below that of the more soluble form, the depression of freezing point by the two together approximating to the sum of the individual depressions. In the case of camphoric anhydride, for example, the *d*-form alone gave a depression of 0.991° ; the *d*- and *l*-forms together, a depression of 1.787° . The method has already been used in connexion with some of Chattaway's polymorphous substances and certain derivatives of cryptopine, to be described by W. H. Perkin. The method has the great advantage that, as it takes only a few minutes to carry out at a low temperature, the probability of the two forms (if indeed

²³ N. V. Sidgwick, *T.*, 1915, **107**, 672; G. Bruni claims priority, *A.*, ii, 827.

they are not polymorphous) coming to tautomeric equilibrium in the course of the experiment is greatly diminished.

The effect of pressure on the polymorphous temperature, as also on the melting point, of some thirty compounds has been investigated by Bridgman²⁴ with an apparatus allowing of the employment of a pressure of 12,000 kilograms per sq. cm. The results are epitomised in a series of curves, and prove that the phenomena of polymorphism are extremely complicated; although in most cases an increase of pressure either steadily raises or lowers the transition temperature, there are others, as, for example, mercuric iodide, in which the curve rises to a maximum and then falls without betraying any discontinuity.

Two papers by Chattaway and Lambert²⁵ on the polymorphism of certain organic compounds are of a special interest. The first contains a description of the monotropic *p*-bromoacetanilide and 2:4-dibromoacetanilide. It is shown that both these compounds are particularly suitable for demonstration or lecture purposes. The behaviour of the two substances is much the same; on allowing a beaker of an alcoholic solution to cool, a copious formation of the labile modification takes place. The crystals consist of fine needles, and are so bulky as to fill the vessel completely. After some time compact crystals of the stable form make their appearance at the top of the mass, and, growing at the expense of the needles, gradually sink down to the bottom of the beaker. The various stages are illustrated by an excellent series of photographs. The suggestion is made that some of the accepted examples of monotropism may really be cases of enantiotropism with a low transition temperature. The second paper relates to some new examples of enantiotropism, and incidentally contains the first recorded experimental verification of a law originally deduced by van't Hoff concerning the relative solubilities of reversible modifications in different solvents.

Enantiomorphism.

With the possible exception of the puzzling element nitrogen, the history of stereochemistry has been mainly occupied with the exploitation of the original tetrahedral hypothesis of carbon valencies and its logical application to other quadrivalent elements. It is only quite recently that we owe a new departure to the genius of Werner,²⁶ who has enriched chemistry with an entirely novel theory of chemical constitution, embodying the co-ordination of a

²⁴ P. W. Bridgman, *Proc. Nat. Acad. Sci.*, 1915, 1, 513.

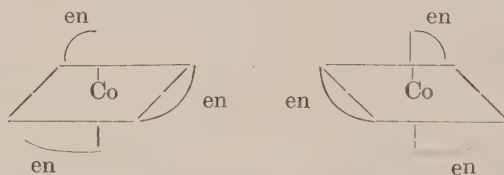
²⁵ F. D. Chattaway and W. J. Lambert, *T.*, 1915, 107, 1766, 1773.

²⁶ A. Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" (1913).

number of atoms or groups round a central nucleus by virtue of subsidiary valencies. The co-ordination number is generally four or six; the first alternative needs no special comment, inasmuch as the arrangement is probably tetrahedral. In hexa-co-ordinated compounds, however, the special arrangement has had to be deduced *de novo*, and Werner has demonstrated with a high degree of certainty that the groups are arranged round the central atom at the six corners of an octahedron. The octahedral structure necessarily introduces new possibilities of isomerism and, more particularly, molecular enantiomorphism. One property of the arrangement may be noted; the higher symmetry of the octahedron, as compared with the tetrahedron, allows of a highly symmetrical type of enantiomorphism. Thus, in the luteotriethylenediamine cobaltic salts of the general formula $[\text{Co en}_3]\text{X}_3$, in which en is the conventional abbreviation of the symmetrical group



and X any acidic group, the positive ion $[\text{Co en}_3]$ can exist in the two enantiomorphous configurations indicated below, formulæ which exhibit the symmetry of the quartz class:



The crystallographic examination of a number of optically active compounds of the above series has been undertaken by Jaeger²⁷ with the following results. The perchlorate and nitrate, $[\text{Co en}_3](\text{ClO}_4)_3$ and $[\text{Co en}_3](\text{NO}_3)_3$, both crystallise in the rhombic system, and clearly show a hemihedral or sphenoidal development.

On the other hand, the optically active bromides (and chlorides) crystallise with two molecules of water in the tetragonal system; there is no geometrical sign of hemihedrism, and the result of etching experiments also agree with holohedral symmetry. The same failure to prove anything but holohedral symmetry attended the investigation of the optically active rhombic iodides, $[\text{Co en}_3]\text{I}_3 \cdot \text{H}_2\text{O}$, and the anhydrous thiocyanates, $[\text{Co en}_3](\text{CNS})_3$. After stating that it is dogmatic to accept the Pasteur principle in view of the present work, Jaeger raises the question whether it is not possible for these highly symmetrical, enantiomorphous molecules to yield a holohedral structure, which shall nevertheless rotate the plane of

²⁷ F. M. Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1217; **18**, 1; *A.*, ii, 399.

polarised light by virtue of the enantiomorphism of the component molecules, and he considers that his facts establish the possibility.*

The number of biaxial crystals of proved rotatory power is steadily increasing. The rhombic, bisphenoidal magnesium salt of *l*-malic acid, $C_4H_4O_5Mg \cdot 5H_2O$, has a rotatory power of -12° for sodium light, whilst *l*-asparagine gave the value -67° (1 cm. thickness in both cases).²⁸ The rotatory dispersions are moderate. The latest addition is lithium sulphate, $Li_2SO_4 \cdot H_2O$, a well-known example of the enantiomorphous class of the monoclinic system.²⁹ The axial plane is perpendicular to (010), and the expectation that the rotatory power should have equal values along the two axes was realised. The mean value for 1 mm. thickness is $1^\circ 48' \pm 39'$ (Na light). In a dextrorotatory crystal the analogous pyroelectric pole lies at the positive end of the symmetry axis. A notable item of the paper is a description of a new mechanical arrangement for obtaining perfect crystals at any constant temperature. It is interesting to note that the rotatory power of lithium sulphate was anticipated by Barker and Marsh,³⁰ who suggested for the salt a spacial configuration founded on the constitutional formula $[SO_3(OH)_2]Li_2$.

In a brief paper by Barlow and Pope³¹ it is pointed out that

²⁸ V. V. Karandéev, "The Measurement of Rotary Power in Biaxial Crystals"—Russian (1913).

²⁹ A. Johnsen, *Centr. Min.*, 1915, 233.

³⁰ T. V. Barker and J. E. Marsh, *T.*, 1913, 103, 837.

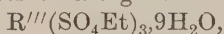
³¹ W. Barlow and W. J. Pope, *T.*, 1915, 107, 700; *A.*, ii, 527.

* Those who are familiar with the history of stereochemistry will recognise that Jaeger's conclusions amount to a re-opening of the Walden-Traube controversy. Whilst expressing the view that Jaeger's work on the perchlorates and nitrates must acquire historical importance, the writer of this Report must say that both the experimental evidence and the theoretical conclusions relating to the bromides, iodides, and thiocyanates leave something to be desired. The general forms (*hkl*) were only developed in the single case of the thiocyanates. In the diagram of the *d*-crystal they are presented holohedrally as very small facets; but in the case of the *l*-crystal the forms $o\{121\}$ and $w\{1\bar{1}1\}$ are actually drawn hemihedrally. The evidence with regard to the remaining compounds consists of etch figures; but such figures can be symmetrical for the same structural causes which operate in the production of a holohedral form. Moreover, added to these matters of detail, there is a general difficulty (which is insurmountable, unless anyone is willing to transform fundamentally the question at issue by subscribing to the view that optical activity is to be expected in a non-enantiomorphous structure). Jaeger's crystals are optically active, as far as he probed the matter. If this optical activity is not due to the enantiomorphous crystal structure (Jaeger's contention), it must be due to enantiomorphism of the molecule. Enantiomorphous molecules (all *dextro* or all *laevo*), however, can not be built together to yield a holohedral crystal structure.

Barker and Marsh³⁰ have fallen into an error in concluding that any optical activity in a biaxial crystal must necessarily be attributed to an enantiomorphous configuration of the chemical molecule, for it is possible to conceive homogeneous assemblages of atomic centres, which, although enantiomorphous as a whole, are, nevertheless, partitionable into non-enantiomorphous molecular groups of atoms. As examples are quoted those assemblages in which it is possible to trace spiral axes that are simultaneously digonal for one kind of atomic centre and tetragonal or hexagonal for another kind.

Isomorphism.

Two papers are to be noted, one by Jaeger,³² the other by Tutton.³³ Jaeger's researches refer to the isomorphous group of rare earth ethyl sulphates of the general formula



in which R''' represents yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, thulium, and neo-ytterbium. The crystallisation is hexagonal, the symmetry that of apatite—as was indicated by a Laue radiogram and etch-figures. The crystals were very well developed and the angles trustworthy; the deviations in going from one salt to another are only a matter of a few minutes, so that the probable value $c:a=0.5062 \pm 0.0012$ can be accepted for the whole series. The molecular volumes, however, are distinctive, so that the individuality of each salt reappears in the form of topic axes. The corresponding compounds of indium and scandium do not belong to the same series, and in order to probe their crystallographic relationships more fully the author prepared and examined acetylacetonates of scandium, indium, aluminium, ferric iron, and glucinum, and found that the first three metals produce an isomorphous series. The monoclinic glucinum compound exhibits such extraordinarily high dispersion of both optic axes and principal optic directions as have probably never been observed in any other compound.

Exception to some of Jaeger's theoretical conclusions has been taken by Tutton, who shows that the above work does not in the least invalidate the conclusions derived from twenty years' work on the simple and double sulphates and selenates. At least three factors operate towards the extreme closeness in the angular values observed by Jaeger: (1) small variations of the atomic weights concerned, (2) the mass effect of the remainder of the molecule,

³² F. M. Jaeger, *Rec. trav. chim.*, 1914, **23**, 343; *A.*, 1914, i, 797.

³³ A. E. H. Tutton, *Phil. Trans.*, 1915, [A], **216**, 1; *A.*, 1916, ii, 38.

(3) the high symmetry of the hexagonal system. Jaeger's results are therefore to be expected. Tutton's paper is mainly occupied with the systematic, morphological, and optical examination of the salts $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, in which M denotes nickel, cobalt, manganese, copper, and cadmium. The general results of the work are now so well known that it need only be stated that the present results amply confirm all previous deductions concerning the crystallographic position of ammonium in the alkali series.

Morphotropy.

Certain new morphotropic relationships among compounds of cyclic structure are discussed in a recent paper by Groth,³⁴ who, it will be remembered, was the first to call attention to the desirability of investigating closely allied organic series of compounds with a view to discover any laws which might govern the mutual replacement of simple radicles. Full use is made of topic axes in order to emphasise the quantitative side of the following resemblances:

	χ .	ψ .	ω .	β .
Imide of succinic acid...	3.193	: 4.048	: 5.527	: 90°0'
Imide of <i>s</i> -dimethylsuccinic acid.....	3.982	: 4.381	: 5.762	: 100 10
Imide of tetramethylsuccinic acid.....	3.415	: 5.425	: 7.063	: 92 8

A comparison of the above values is believed to lay bare certain morphotropic regularities due to the regular type of chemical replacement. Now the stock example of this kind of regular progression is that given below, in which there would seem to be a progressive alteration of the crystal structure when hydrogen is replaced by methyl, ethyl, and propyl groups:

	$a : b : c$	χ .	ψ .	ω .
NH_4I	1 : 1 : 1	3.860	3.860	3.860
NMe_4I	1 : 1 : 0.7223	5.319	5.319	3.842
NEt_4I	1 : 1 : 0.5544	6.648	6.648	3.686
NPr_4I	0.776 : 1 : 0.6283	6.093	7.851	4.933

It has, however, been recently urged by Barlow and Pope³⁵ that the indices {100} and {111} of the tetramethyl compound should be replaced by {110} and {101}, the justification being that the new indices are simpler and a much better reflection of the dodecahedral habit of the crystals. The proposed change involves a modification of the ratio $c:a$ by the amount $\sqrt{2}$; the new value becomes 1.0214, and indicates pseudo-cubism. It is then concluded that topic axes are of little or no value in morphotropic comparisons;

³⁴ P. Groth, *Zeitsch. Kryst. Min.*, 1915, **54**, 498.

³⁵ W. Barlow and W. J. Pope, *Phil. Mag.*, 1915, [vi], **29**, 745; *A.*, ii, 427.

the geometrical constants of some twelve substances, chemically allied to ammonium iodide, are passed in review, the final conclusion being that all the structures concerned are pseudo-cubic.

The divergent views indicated above merit a little discussion, since they bear on the general subject of crystal morphology. It may be observed that Groth was guided by cleavage in the choice he made of the alternative methods of describing the tetragonal compound. The only reason Barlow and Pope give for changing the setting is "simplicity of indices."* The connexion between indices and crystal structure deserves a little examination.

In text-books it is generally stated that the fundamental law of geometrical crystallography is the law of rational intercepts or indices. However true this may be, it is, nevertheless, not the law of morphological crystallography. The law of rational indices contains no limitations on the number and nature of faces actually developed on a crystal; for example, the law will allow of crystals being "spheres," since a sphere can be regarded as a myriad of plane faces having the general indices $\{\infty - m, \infty - n, \infty - p\}$, in which ∞ is meant to connote a very large number as compared with m , n , and p . Fortunately, observations show that crystals are bounded by a certain number of plane faces; to treat crystallography as a purely geometrical problem is to shut one's eyes to the main facts of the science.

It is frequently added as a corollary in the text-books that the indices are simple numbers. This marks a real advance, but it is still unsatisfactory unless it is simultaneously pointed out that simplicity of indices largely depends on a happy choice of axial directions A , B , C . The anorthic isomorphous series, typified by ethylenediamine manganese sulphate, $\text{C}_2\text{H}_4(\text{NH}_3)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, as described by Rosický,³⁶ has the form development: (010) , (110) , $(\bar{1}\bar{1}0)$, (001) , (133) , $(\bar{1}\bar{3}3)$, $(4:\bar{1}\bar{2}:3)$, $(4:12:3)$, (263) , $(\bar{2}\bar{6}3)$, $(\bar{8}03)$, $(8:24:\bar{3})$. These complicated indices by a suitable transformation become term for term $(\bar{1}10)$, $(\bar{1}01)$, $(0\bar{1}1)$, (111) , (011) , (101) , $(11\bar{1})$, $(\bar{1}11)$, (010) , (100) , $(11\bar{1})$, (311) .

The question as to how far a crystal obeys a law of simple indices can only be quantitatively probed if we can decide on a measure of simplicity; whether, for example, simplicity is to be measured by the actual summation of indices or of the indices squared. In his

³⁶ V. Rosický, *Zeitsch. Kryst. Min.*, 1909, **46**, 357; *A.*, 1909, **i**, 458.

* They would, however, seem to think that it is not necessary to adhere to this principle throughout the whole of their paper; for in subsequent attempts to support their thesis of pseudo-cubism they have recourse in some three cases to a multiplication or division of an axial ratio by 2, a procedure which leads to complicated indices.

comprehensive examination of this question, Fedorov³⁷ adopted the latter criterion. As a result of this work it must be concluded that crystal morphology does agree, in the main, with the principle of simple indices—provided the descriptive conventionalities now in vogue are mercilessly discarded. In the rhombic system, for example, one must be willing to adopt no fewer than four systems of selecting the axial directions A , B , C ; one must also be prepared to adopt a system of four axes and indices, not merely in hexagonally developed crystals, like quartz, belonging to the hexagonal-rhombohedral system, but also in certain crystals of the rhombic, monoclinic, and anorthic systems. The proviso first mentioned actually leads to great confusion, for faces of the same form may acquire totally different indices. Whilst adopting a judicious use of the hexagonal form of indices (for crystals of the “hypo-hexagonal type”), Fedorov shrank from carrying through the principle to its logical conclusion.

A rigorous employment of this principle of simple indices is really a purely morphological question—that is to say, it need have no reference to the structure, but if we bear in mind that the geometrical axes A , B , C , thus located, must be identical with certain structural directions of the lattice, we see that the selection of a standard set of axial directions and ratios, $a:b:c$, by means of the principle of simple indices, is practically equivalent with the discrimination of crystal structure by means of the Bravais principle. The sole difference lies in (generally small) quantitative details; in the cubic system the two methods are identical. The principle of indices could never be regarded by a crystallographer as anything but provisional; it was therefore a logical step to substitute for it a structural conception like reticular density or area, especially as the substitution greatly lightens the actual process of analysis of crystal morphology; for example, there need be no recourse to four distinct selections of A , B , C in a rhombic crystal. Fedorov³⁸ foreshadowed this substitution in the year 1903.

Simultaneously, but quite independently, Friedel^{39, 40} was examining morphology in the light of the Bravais principle. In an extremely important series of papers, which appear to have attracted little, if any, attention, Friedel demonstrated that crystal faces can be regarded as due to the development of the most highly beset planes of the structural lattice. Although there are frequent examples in which anticipated planes are not actually observed,

³⁷ E. S. Fedorov, various papers in *Zeitsch. Kryst. Min.*, 1902–1903.

³⁸ *Ibid.*, 1903, **38**, 321.

³⁹ G. Friedel, “*Étude sur les groupements cristallins*” (1904).

⁴⁰ *Bull. Soc. franç. Min.*, 1907, **30**, 326; 1908, **31**, 5.

there is, nevertheless, a remarkable agreement on the whole. A cursory inspection of Friedel's studies will reveal the fact that the order of reticular densities does not in general follow the order of simplicity of the indices allotted to the faces. This is partly due to his adoption of the conventional rules for selecting *A*, *B*, *C*; the want of harmony is, naturally, especially marked in pseudo-hexagonal crystals.

The work of Fedorov and Friedel is so recent that it has not had time to make itself felt in crystallography. It serves to accentuate the truth that the work of the average morphologist is superficial. The measurer of crystals has been content to fall back on the great latitude allowed by the law of rational indices, even when he is occupied in such ambitious work as deducing morphotropic resemblances. It is surely obvious that such work has no exact meaning or consequence when no effort has been made to analyse the morphological data and so circumscribe the infinite number of possibilities allowed by the law of rational indices. Whether the resemblances or comparisons are expressed in terms of axial ratios, topic axes, or equivalent parameters has no bearing on the point at issue. Cogency, of course, is not to be denied to all the published resemblances. In absence of any experimental method of probing crystal structure,* the cogency of a reputed resemblance can only be estimated by the success with which it undergoes the test of the Bravais principle—a principle which, indeed, epitomises the simple relationship between the various faces observed on crystals of some thousands of substances.

With regard to the particular morphotropic resemblances under discussion, the application of the Bravais principle reveals some essential structural differences, for certain lattices are central whilst others are not; to this extent are Barlow and Pope supported in their objection. On the other hand, the principle does not confirm Barlow and Pope's idea of pseudo-cubism. It must be noted that the question of pseudo-cubism has been thoroughly thrashed out by French crystallographers. Both Mallard and Wallerant have in their time subscribed to the view that a good many crystals are pseudo-cubic. The question was finally put at rest by Friedel, who showed that pseudo-cubism is a universal property of crystals, when the structural space lattice is regarded in a purely geometrical sense.

T. V. BARKER.

* It need scarcely be stated that the recent development of X-ray work promises to afford trustworthy experimental evidence. It will, however, probably be some years before the method becomes general in crystallographic laboratories. It is, perhaps, too much to expect the general physicist to acquire an interest in matters of crystallographic detail.

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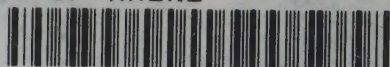
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